Degradation Mechanism and Morphological Change of PET by PEG–Diamine

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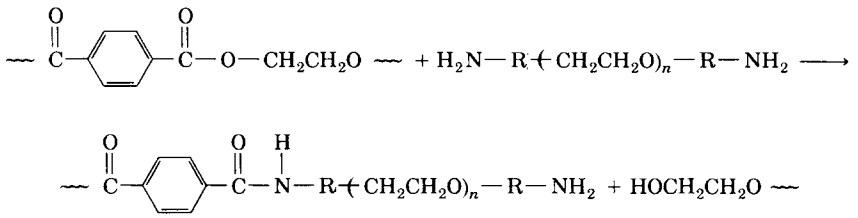
Synopsis

The aminolysis mechanism and morphological change were investigated with NMR, IR, GPC, density, and other physicochemical methods when the biaxially drawn PET film was aminolyzed with PEG–diamine at 130°C. By the aminolysis reaction, the PET chain end was capped with PEG chain as the following equation:



Molecular weight showed a rapid decreasing tendency in the initial stages of the aminolysis reaction. The crystallinity, measured by density and IR methods, increased with the reaction time mainly due to the recrystallization of the amorphous PET chain promoted by better chain mobility of the PEG-terminated PET. The fold period of the chain-folded lamellar crystal formed through recrystallization was the same as that of the original PET lamellar crystal. It was found that 74% of all the capped PEG chains were located in the amorphous region, 18.4% at the initial point from which the recrystallized lamellar crystal began to grow, and the rest in the lamellar crystalline lattice.

INTRODUCTION

Since the aminolysis reaction of esters by amines was first reviewed by Arnett et al.[1] many investigators have reported the aminolysis reaction of PET by alkylamines, guanidine, etc.[2–18] All of these reports can be divided largely into two fields, i.e., study of PET morphology and application of the aminolysis to the practical uses.

Farrow et al.[2] found that the rapid initial degradation slowed down and extensive crystalline material, the crystallinity of which failed to exceed 72%, remained. Kurita[3] reported much the same results. He detected lamellae and lamellae plus fibrillar structure in undrawn and drawn PET, respectively, by using ethylamine as an etchant. Overton and Haynes,[4] Metha and Bell,[5] and Duong and Bell[6] showed that the average fold period of PET lamellae ranged

Journal of Applied Polymer Science, Vol. 37, 2855–2871 (1989)

CCC 0021-8995/89/102855-17$04.00

from 6 to 9 repeating units depending on the annealing condition by analyzing the aminonlyzed residues with GPC. In the first structural study on the aminolyzed PET, Baker[7] reported that patterns of parallel lines and "brick" structure were formed by *n*-propylamine on the surface of one-way drawn PET and two-way drawn heat set PET, respectively. He suggested that the distribution of these micron-size structures was related to the strain distribution incurred during drawing. Chu and Wilkes[8] and Adams[9] investigated the bulk morphology of PET films and fibers using *n*-propylamine as a chemical etchant. SEM showed a surface network structure along etched samples, and the nature of this network was dependent on the mechanical and thermal history of the specimen. Abe and Sakamoto,[10,11] Sekine et al.[12,13] and Sakami[14] showed also the same results. They separated skin from the core structure of the drawn PET fiber and separated the biaxially stretched PET film into skin and core phases using aqueous ethylamine. Sweet and Bell[15] and Yamazaki and Tonami[16] reported that certain aqueous amine solutions crystallized and degraded PET simultaneously. They concluded that solvent-induced recrystallization during aminolysis was deeply related to the concentrations of amines and their solubility parameters.

Aminolysis has many practical applications, i.e., improvement of softness, antipilling, ease of dyeability, hydrophilicity, etc. There have been some patents and theses.[19-25] However, no one has been entirely successful in applying the aminolysis to practical purposes, as a severe decrease in molecular weight and mechanical strength is inevitable as long as the lower alkylamines are adopted as a PET modifier. It is well known that such a severe reduction of molecular weight is caused by the selective degradation of amorphous region including tie chains and/or folded chain regions as previously referred to.[18,26] If we use the high molecular weight amine as a PET modifier, it is easily assumed that the larger steric effect of this amine would reduce the selectivity in its chemical attack on ordered and unordered PET regions and not give a severe molecular weight reduction. In this case, however, it is expected to increase the aminolysis temperature because of low basicity, high steric effect, and low diffusivity in order to obtain the moderate aminolysis reaction rate.

In our previous reports,[27,28] the PEG–diamine, which is expected to have good antistatic properties and hydrophilicity as it contains PEG with molecular weight of nearly 600, was employed to improve the hydrophilic properties of PET films and fibers without a severe reduction of molecular weight and mechanical strength. We reported that PET chain ends were blocked with PEG as a result of the aminolysis reaction of the ester bond of PET by the amine radical of PEG–diamine at 130°C. The PEG–diamine-treated PET showed very good water-wicking, oily soil releasing, and antistatic properties. But we did not examine the exact mechanism of PET aminolysis by PEG–diamine and the changes in molecular weight and morphology during reaction in the earlier reports. Since it is very important in engineering applications to find out whether the aminolysis of PET by PEG–diamine can be truly utilized as a practical process to impart the durable hydrophilicity to PET or not, we tried to investigate the changes in molecular weight and morphology during and after the aminolysis and to elucidate the exact aminolysis mecha-

nism of PET by PEG–diamine in this report. The present study is initiated as a consequence of additional results found in our previous works.[27,28]

EXPERIMENTAL

Materials

The biaxially drawn PET film and PEG–diamine (Jeffamine ED-600) were kindly supplied from Sun Kyung Synthetic Fiber Co., Korea and Texaco Chemical Co., respectively. The film was 24 μm thick. An intrinsic viscosity of 0.899 was found from a solution of PET in 1,1,2,2-tetrachloroethane and phenol (1 : 1 v/v) at 25°C. The density of the initial film was 1.398 g/cm^3, determined from density-gradient analysis. The chemical structure of PEG–diamine employed here is as follows:

$$H_2NCHCH_2(OCHCH_2)_a(OCH_2CH_2)_b(OCH_2CH)_cNH_2$$
$$\quad\;\;|\qquad\quad|\qquad\qquad\qquad\qquad\quad|$$
$$\quad CH_3\qquad CH_3\qquad\qquad\qquad\qquad CH_3$$

$$(a + c = 3.5 \text{ and } b = 13.5)$$

Aminolysis

Since PEG–diamine has low basicity, high steric hindrance, and low diffusivity due to its high molecular weight, the degradation rate of PET by PEG–diamine is expected to be very slow at room temperature. This is the temperature normally adopted for the aminolysis of PET by low molecular weight amines such as methylamine, ethylamine, and propylamine. Therefore, we employed a reaction temperature of 130°C, which is above T_g of PET, in order to increase the diffusivity and aminolysis rate. Above this temperature, PEG–diamine was found to be thermally unstable. After the desired reaction time, the residual PET film was isolated, washed in water, and dried in air. The sample code for the aminolyzed PET is expressed as J-t, where t represents aminolysis time (h).

Annealing

The PET film was annealed in pure PEG-600 at 130°C for varying lengths of time. After the desired annealing time, the PET film was isolated, washed in water, and dried in air. The sample code for the annealed PET is expressed as P-t, where t represents annealing time (h).

NMR Measurement

Proton NMR spectra were obtained with an 80 MHz FT-NMR spectrometer (Model FT-80A, Varian) with trifluoroacetic acid-d_1 as a solvent. The number of scans ranged from 20 to 200.

IR Measurement

The IR spectra were recorded using a Nicolet MX-1 FTIR spectrometer and stored on magnetic disk for further use. All spectra were recorded at 1 cm^{-1} resolution with 32 scans, and all subtractions were carried out using the following equation:

difference spectrum = sample spectrum − (scale factor) × reference spectrum

Density Measurement

Densities of specimens were measured with a density gradient column containing *n*-heptan and carbon tetrachloride at 20.0 ± 0.2°C.

GPC Measurement

Molecular weight distribution of aminolyzed PET sample was determined by means of a Waters Model 244 gel permeation chromatograph. The unit with columns consisting of four different pore-sized—500, 10^3, 10^4, and 10^5 Å —Styragels was operated at room temperature, using chloroform and *o*-chloro phenol mixture (1 : 4 v/v) as an eluent. The system was calibrated with polystyrene standards having molecular weights of 2.7×10^6, 2.33×10^5, 3.5×10^4, 8.5×10^3, and 2.9×10^3, respectively.

RESULTS AND DISCUSSION

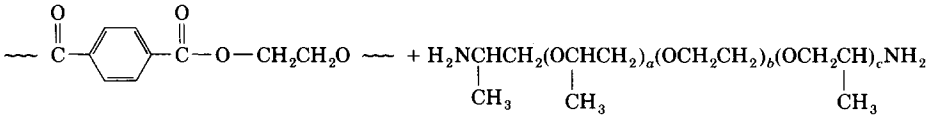
Reaction of PEG–Diamine with PET

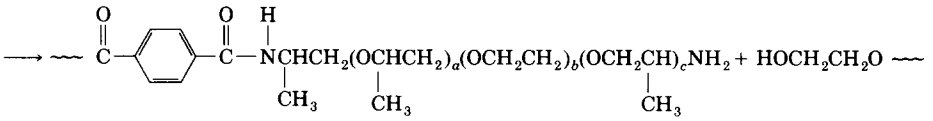
The IR spectra of control sample PET, P-24, and J-24 are shown in Figure 1. A comparison of control PET and P-24 assures that there was no chemical reaction and very little effect of annealing on P-24. However, the IR spectrum of J-24 shows that new bands exist near 1540 cm^{-1} assigned to amide II, the intensities of the 849, 1386, and 1471 cm^{-1} peaks associated with *trans* isomer have increased, and the *gauche* isomer bands near 898, 1173, 1370, and 1456 cm^{-1} have decreased in intensity. These changes of J-24 indicate that the amide bond was newly formed as a result of the reaction of the ester bond of PET with PEG–diamine, and there are many *gauche–trans* isomerizations during the aminolysis; thus the crystallinity has increased. The cause of *gauche–trans* isomerization in J-series will be discussed in a later section.

The conformational and chemical changes in J-24 occurring during aminolysis cannot be investigated precisely until the difference spectrum is obtained by subtracting the pure PET component from the IR spectrum of J-24 and its absorbance peaks are identified. The difference spectrum may be obtained by subtracting these two spectra on a 1 : 1 basis using an internal thickness band[29] at 793.5 cm^{-1}. In this case the reference spectrum must be the IR spectrum of P-24 in order to find the conformational and chemical change excluding annealing effect during aminolysis of PET by PEG–diamine. The difference spectrum was obtained by subtracting the IR spectrum of P-24 from that of J-24 until the 793.5 cm^{-1} peak was reduced to the base line. It is

shown in Figure 1(d). As seen here, the new bands have occurred at 1655 ± 5 (amide I), 1540 ± 5 (amide II), 1103 ± 1, and 1074 ± 2 cm^{-1}. The last two peaks are assigned to the asymmetric C—O—C stretching of the PEG unit.

In the NMR spectrum of PEG–diamine, the singlet at 3.6 ppm is assigned to the methylene group of ethylene oxide and propylene oxide units, the broad multiplet near 3.3 ppm to the methine group, and the multiplet near 1.1 ppm to the methyl group. The singlet at 8.2 and 4.6 ppm in the NMR spectrum of control PET are for phenylene and ethylene groups, respectively. The occurrence of the singlet at 3.6 ppm and the doublet at 1.2 ppm in the NMR spectrum of J-24 and the IR results indicate that the aminolysis of PET by PEG–diamine takes place according to the following chemical reaction:





i.e., the PET chain end is capped or blocked with PEG–diamine as a result of the aminolysis reaction of the ester bond of PET by the primary amine radical of PEG–diamine.

Changes in PEG Content with Aminolysis Time

The content of PEG in the PEG–diamine-treated samples is calculated from the following equation:

$$\text{PEG content (wt \%)} = \frac{48.398B}{192A + 48.398B} \times 100$$

where A and B are the areas of the singlets at 4.6 and 3.6 ppm in the NMR spectra, respectively.

In the initial aminolysis stage, the PEG content has increased rapidly with time, but after 3 h, a steady increase was observed. This slow increase of PEG content after 3 h may be attributed to the difficulty of diffusion of PEG–diamine into the inside of the PET film owing to its large steric hindrance.

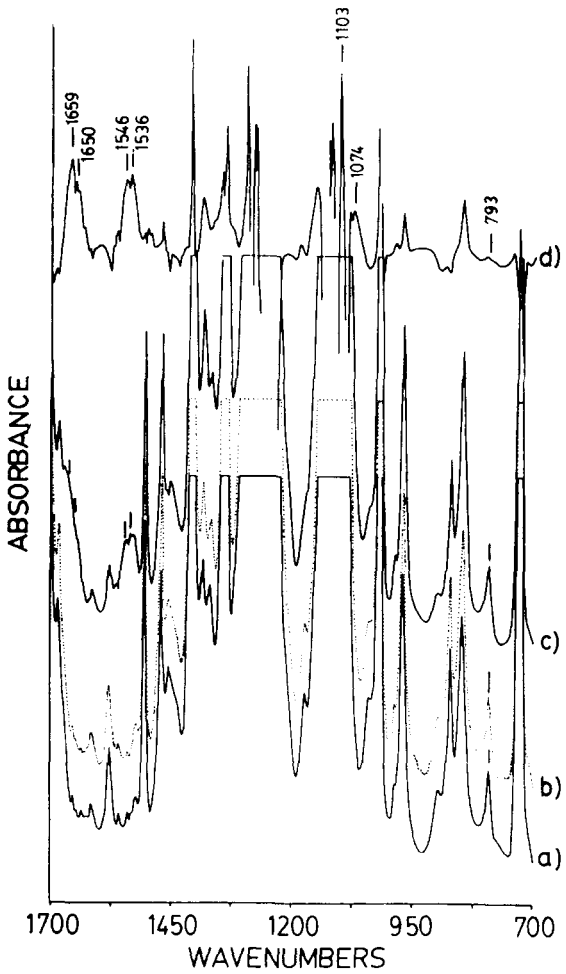


Fig. 1. Absorbance spectra of control PET, P-24, and J-24 and difference spectrum obtained from J-24 minus P-24: (a) control PET, (b) P-24; (c) J-24; (d) J-24 minus P-24.

Experimental data on the change in PEG wt % may be correlated as wt % = $2.1147 \times t^{0.4593}$, where time t is in hours.

Changes in Molecular Weight

Figure 2 shows the changes in $\overline{M}_n$, $\overline{M}_w$, and polydispersity index of PET aminolyzed with PEG–diamine against aminolysis time. There is a rapid fall in molecular weight up to the aminolysis time of 3 h, after which molecular weight reduces very slowly. The rapid reduction in molecular weight and polydispersity index in the initial stage and the very slow reduction in the later stage suggest that there can be a selective degradation in amorphous and/or chain-folded regions as in the case of aminolysis of PET by the lower alkylamines such as methylamine and ethylamine.

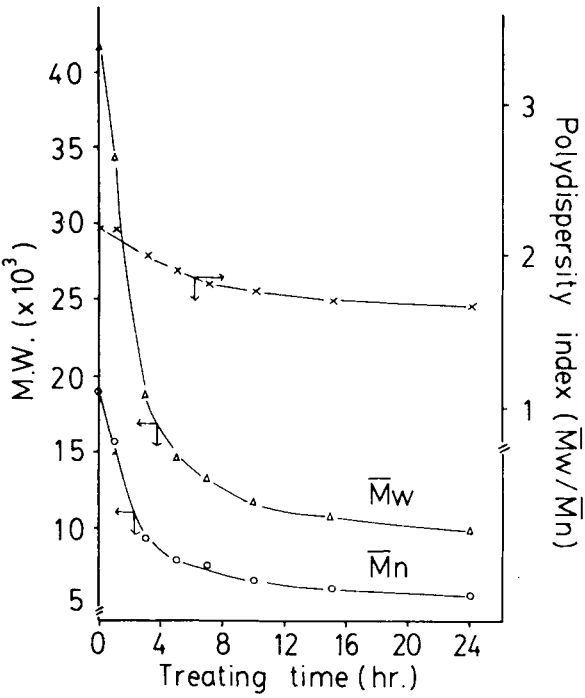


Fig. 2. Changes in $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_w/\overline{M}_n$ of PET treated with PEG-diamine at 130°C with treating time.

Changes in Crystallinity

Provided that the density of PEG-diamine in J-t's is the same as in the original bulk state, the density of pure PET component after aminolysis can be calculated from the following equation:

$$d_{\text{adj}} = \frac{100 - W}{100/d_{\text{meas}} - W/1.04355}$$

where d_{adj} is the density of pure PET component, d_{meas} is the measured density, W is the weight percentage of PEG, and 1.04355 is the density of PEG-diamine at 20°C. Thus the volume percentage crystallinity of samples was calculated from the following equation:

$$X_{c,v}(\%) = \frac{d_{\text{adj}} - d_{\text{am}}}{d_{\text{cr}} - d_{\text{am}}} \times 100$$

where the quantities d_{am} and d_{cr} represent the amorphous density (1.355 g/cm^3) and the crystalline density of PET (= 1.477 g/cm^3),[30] respectively.

Figure 3 shows changes in the crystallinity of P-t's and the crystallinity calculated from the adjusted density of J-t's with annealing time or aminolysis time. The increase in the crystallinity for the annealed PET was negligible, while the crystallinity of PET aminolyzed with PEG-diamine has

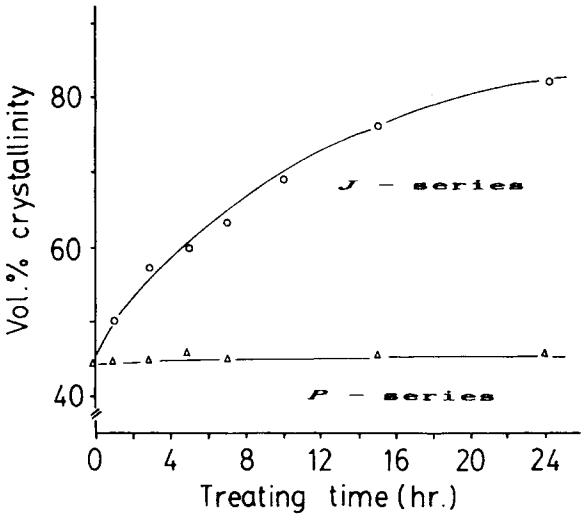


Fig. 3. Changes in vol % crystallinties of PET only annealed and treated with PEG–diamine at 130°C with treating time.

increased rapidly with aminolysis time. Sample J-24 was found to have a crystallinity of as much as 83%.

In addition to density measurements, the crystallinity of a polymer material can be measured with WAXD[31-33] and IR spectroscopy.[34-36] WAXD cannot be used in comparing specimens, having very slight differences in crystallinity, due to systematic errors arising from the low signal/noise ratio of the X-ray diffractogram of an imperfect semicrystalline organic polymer. Density measurements cannot be applied to determine the exact crystallinity of the polymer material containing some additives such as delustrants, nucleating agents, and plasticizers, since it would be impossible to calculate the density of the pure polymer portion from the measured density without the knowledge of the densities of the additives. Therefore, some researchers recommend IR spectroscopy to determine the crystallinity of these polymeric products.

Aharoni et al.[36] found that the 1578 cm^{-1} band, associated with an in-plane ring C—C stretch, is insensitive to the development of crystallinity in PET samples. The band at 973 cm^{-1} is assigned to an asymmetric C—O stretch and is associated with the *trans* conformation of the —O—C—C—O— group along the PET chain. Its intensity is very sensitive to the development of order in PET. They have reported that percent crystallinity based on IR data can be calculated from the absorbance ratio $A_{973\ cm^{-1}}/A_{1578\ cm^{-1}} = 0.0378/1\%$ of crystallinity. In this report, IR crystallinity was determined according to Aharoni's method.

Figure 4 shows the changes in IR crystallinity of P- and J-series samples with treating time. Comparison of IR determined crystallinity and volume percentage crystallinity measured by density shows that the two results coincide with each other in the changing tendency with treating time, although there is a small difference between the absolute values from these two methods. As in the case of the changes in volume percentage crystallinity

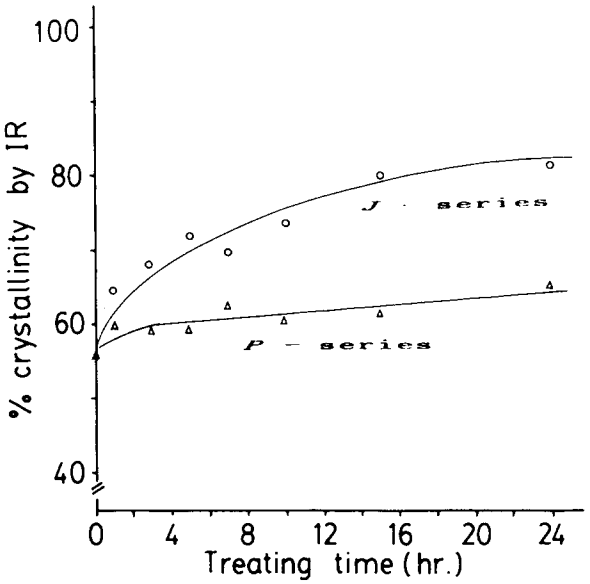


Fig. 4. Changes in IR % crystallinties of PET only annealed and treated with PEG-diamine at 130°C with treating time.

shown in Figure 3, the increase in IR determined crystallinity of the annealed PET was extremely small, while that of PET aminolyzed with PEG-diamine has increased rapidly with aminolysis time. Upon considering the rapid increase in crystallinity during aminolysis by PEG-diamine, five possible factors may be thought of. They are: (1) a thermal annealing effect during aminolysis, (2) selective degradation of amorphous region, (3) solvent-induced crystallization by the plasticization effect of PEG-diamine diffusing into the inside of PET, (4) nucleation controlled crystallization by the action of the capped PEG chain end as a heterogeneous nucleus, and (5) diffusion-controlled recrystallization by the rapid diffusion of PET chains capped with PEG into the crystal phase owing to the excellent chain mobility of a PEG chain end and its reduced molecular weight.

The annealing effect can hardly be considered to contribute to the increase of the crystallinity of the aminolyzed PET, since there is negligible change in the crystallinity of PET samples with annealing time i.e., P-series as shown in Figures 3 and 4. When the solvent and polymer have similar solubility parameters, the solvent-polymer interactions become significant. These interactions cause an increase in the mobility of the polymeric segments by lowering the secondary intermolecular bonding forces. When the polymer-solvent interactions become strong enough, the polymeric chains may be mobile enough to rearrange into a lower thermodynamic energy state, i.e., a crystalline form. The solubility parameter of PET[15] is 10.7. No value could be found in the literature for PEG-diamine, but the solubility parameter of PEG-diamine can be easily assumed from that of the corresponding PEG. Unfortunately, the solubility parameter of PEG-600 could not be found in the literature, either. However, if the solubility parameters of PET and PEG are of nearly the same value, the crystallinity of the P-series samples

annealed in PEG medium should have been increased with annealing time. Therefore, solvent crystallization by PEG–diamine can be also neglected. Even though some selective degradation in amorphous regions can be expected from observed reduction of molecular weight with aminolysis time, this selective degradation of amorphous regions cannot be the main factor causing the aminolyzed PET to show a significant enhancement in crystallinity because of the difficulty in diffusion of PEG–diamine into the inside of the compact PET film due to steric interference by its high molecular weight. This is not the case of the aminolysis of PET by methylamine or ethylamine. Since the aminolysis temperature is near the cold crystallization temperature of PET, nucleation-controlled crystallization, even with some recrystallization during aminolysis, is less dominant than diffusion-controlled crystallization.[37] If a certain PET chain in the amorphous region has reacted with PEG–diamine and formed a new amide linkage during aminolysis, this PET chain can diffuse easily into the crystal phase owing to the high chain mobility of the PEG chain end and its reduced molecular weight as indicated in the previous section, i.e., the free enthalpy of activation for the transport of the crystallizing unit across the boundary phase is reduced. Accordingly, recrystallization and crystal growth in PET during aminolysis can be assumed to be faster than in PET only subjected to heat treatment. Consequently, one can summarize that the important factors increasing the crystallinity of PET during aminolysis by PEG–diamine are selective degradation in amorphous region and diffusion-controlled recrystallization by the action of the high chain mobility of PEG chain ends.

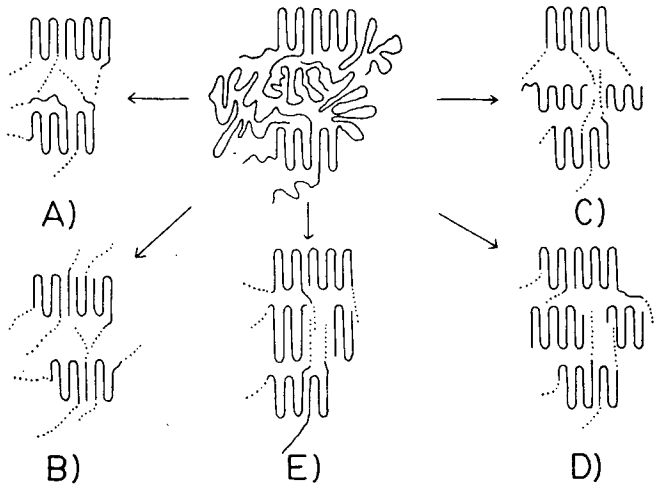
Interpretation of Changes in Morphology during Aminolysis

Interpretation by the IR Spectrum

It is well known that in the amorphous state PET has a *gauche* structure in the ethylene glycol fragment, contrary to the crystalline state where the ethylene glycol fragment of PET has a *trans* structure. All major changes in IR spectra of PET, which are observed upon transition from the amorphous to the crystalline state, have been attributed to this conformational change.[38,39]

As the aminolysis time is increased, the intensities of *trans* conformational bands, i.e., 1471.5 (*trans* CH_2 bending), 972 (*trans* C—O asymmetric stretching), and 848 cm^{-1} (*trans* CH_2 rocking) and the intensity of the 1386 cm^{-1} band (crystal benzene mode) have increased, while the intensities of *gauche* conformational bands, i.e., 1456–1452 (*gauche* CH_2 bending), 1369 (*gauche* CH_2 wagging), 1173 (*gauche* CH_2 twisting), 1042 (*gauche* C—O stretching B mode), and 898 cm^{-1} (*gauche* CH_2 rocking) have decreased. The peaks at 1173 and 1042 cm^{-1} have disappeared after aminolysis of 24 h. For PET subjected only to heat treatment at 130°C, such intensity changes were not observed. Therefore, it can be easily concluded that annealing and solvent-induced crystallization do not cause large increases in the crystallinity of PET when aminolyzed with PEG–diamine, i.e., the annealing effect cannot be considered as one of the important factors to increase the crystallinity of the aminolyzed PET.

Methylamine and guanidine are known to degrade selectively the regular chain fold as well as the amorphous region of PET.[5,18] If PEG-diamine also degrades selectively the regular chain fold as in the case of the aminolysis by methylamine or guanidine, the intensity of the 988 cm^{-1} peak (regular chain fold) must decrease with the increasing aminolysis time. On the contrary, the intensity of 988 cm^{-1} peak has increased with aminolysis time. From this result, it can be also suggested that the amorphous regions are selectively degraded by PEG-diamine and then the chain-folded lamellar crystals are reformed by diffusion controlled crystallization owing to the high chain mobility of PEG-chain end. Figure 5 shows a plot of the ratio $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$ against aminolysis time. This ratio is found to be independent of aminolysis time. This result can be analyzed by schematic models for the degradation and/or recrystallization mechanism shown in Scheme 1:



Scheme 1. Imaginary degradation and/or recrystallation mechanism when PET is treated with PEG-diamine at 130°C. (A) Selective degradation of amorphous region; (B) selective degradation of both amorphous and regular folded-chain regions; (C-D) recrystallization of amorphous region: the recrystallized lamellar crystal has the shorter fold period than the original one (C), the same fold period as the original one (D), and the longer fold period than the original one (E), respectively. (· · ·) PEG-diamine chain; (——) PET chain.

The selective degradation of amorphous regions of PET [Scheme 1(A)] will cause the ratio of $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$ to have a constant value and the selective degradation of both amorphous and regular chain-folded regions [Scheme 1(B)] will bring about a decrease of the ratio $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$. Schemes 1(C), 1(D), and 1(E) show the recrystallization of amorphous PET chain during degradation. The recrystallized lamellar crystal having a shorter fold period than the original one, as shown in scheme 1(C), will produce an increase in the ratio $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$, while the recrystallized lamellar crystal of the longer fold period, as shown in Scheme 1(E), will cause a decrease. If the fold period of the recrystallized lamellar crystal is the same as that of the original one as shown in Scheme 1(D), it will cause the ratio $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$ to have constant value. The independence of this quantity with aminolysis time indicates that the selective degradation of amorphous

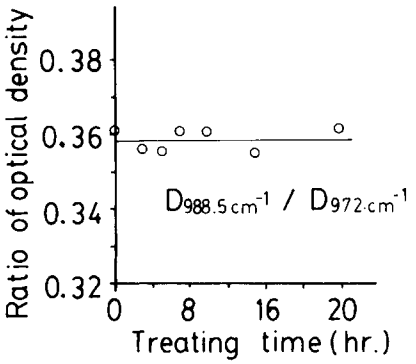


Fig. 5. Change in the intensity ratio of regular folded-chain band to trans conformation band with treating time.

region and/or the reformation of the chain-folded lamellar crystal with fold period the same as that of the original one can occur during aminolysis.

The isolated crystalline component spectrum of PET aminolyzed with PEG–diamine at 130°C is shown in Figure 6(a): it was obtained by digitally subtracting the spectrum of J-5 from that of J-24 until bands associated with the *gauche* conformations (1453 cm^{-1} CH_2 bending, 1369 cm^{-1} CH_2 wagging, 897 cm^{-1} CH_2 rocking) were reduced to the base line. When this was done, the bands at 1042 and 1174 cm^{-1} were also absent. These latter bands have been assigned to the B mode of the *gauche* C—O stretching vibration and the *gauche* CH_2 twisting, respectively.[40] The new crystalline bands at 911, 1224, 1233, and 1683 cm^{-1} are brought out clearly by the subtraction procedure and have not been previously characterized. The isolated amorphous phase spectrum of aminolyzed PET is shown in Figure 6(b), and was obtained by subtracting the spectrum of J-24 from that of J-5 until bands associated with the *trans* conformations and crystal benzene mode (1387 cm^{-1}) were reduced to the base line. One can also note that the 988 cm^{-1} fold band which is clearly evident in the crystalline component spectrum is absent in the amorphous component spectrum. This indicates that the ratio $A_{988\ cm^{-1}}/A_{972\ cm^{-1}}$ has constant value and is independent of aminolysis time, i.e., the selective degradation of amorphous region and/or the reformation of the chain-folded lamellar crystal with the same fold period as in the original PET sample occur during the aminolysis of PET by PEG–diamine at 130°C.

Interpretation by Crystalline Fold Period Measurement

Duong and Bell[6] and Overton and Haynes[4] have reported that the amorphous regions and chain folds in semicrystalline PET film degrade much faster than the crystal lamellae by methylamine, and after more than 8 h of amine treatment they are completely removed by the methylamine. Therefore, the aminolysis by methylamine is very useful for investigating the lamellar morphology of semicrystalline PET. About 150 mg of control PET of J-series specimen was placed in a sealed tube containing 10 mL of 40% aqueous methylamine. After 15 and 24 h of methylamine treatment, the

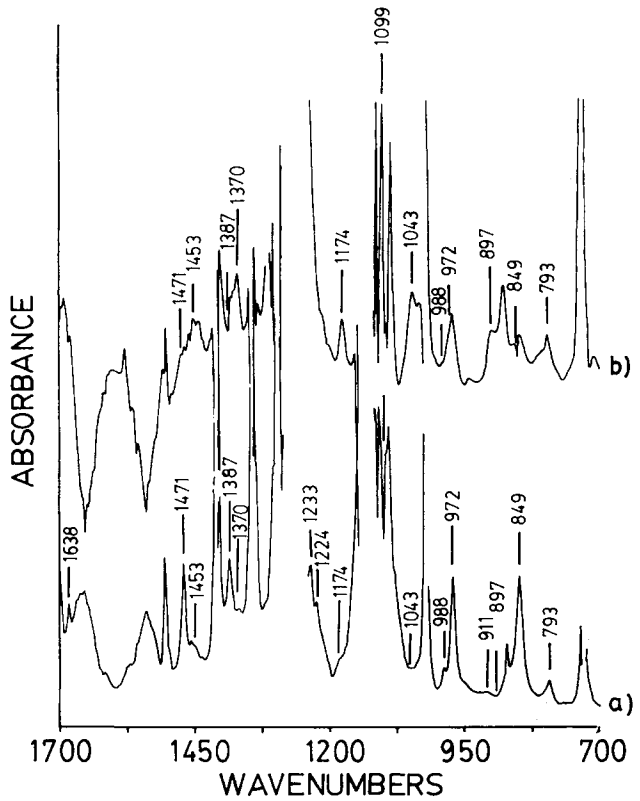


Fig. 6. Difference spectra: (a) J-24 minus J-5, i.e., isolated crystalline component of PET treated with PEG–diamine; (b) J-5 minus J-24, i.e., isolated amorphous component of PET treated with PEG–diamine.

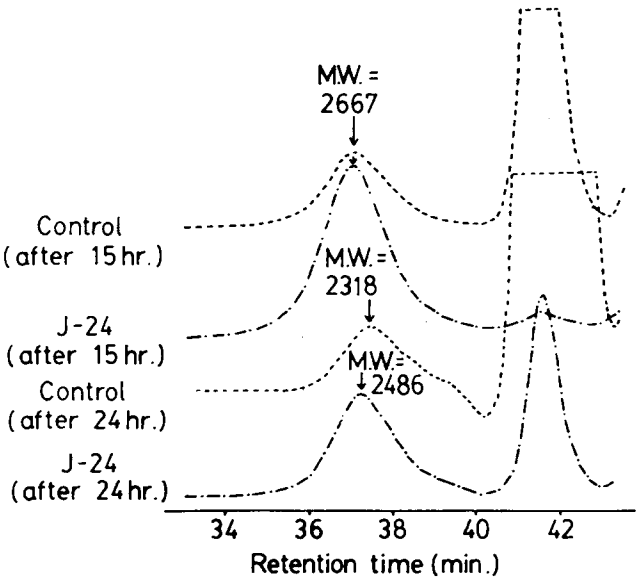


Fig. 7. Gel permeation chromatograms of control PET and J-24 aminolyzed with 40% methylamine solution for 15 and 24 h.

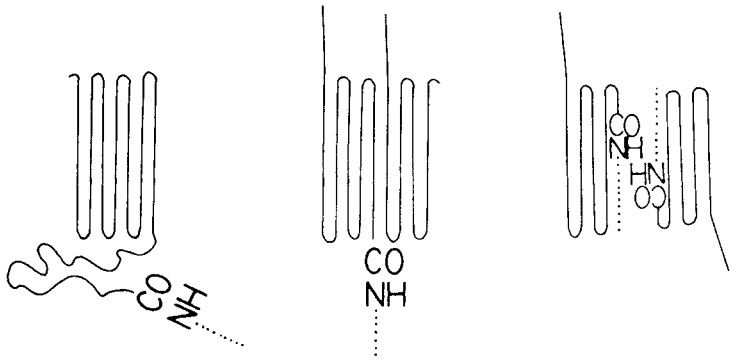
powdered residue was filtered, carefully washed with distilled water, and vacuum-dried for 3 h at 30°C.

Figure 7 shows the gel permeation chromatograms of control PET and J-24 after degradation by 40% aqueous methylamine for 15 and 24 h. The peaks at the left represent the aminolyzed materials with a molecular weight distribution ($\bar{M}_w/\bar{M}_n$) very close to 1.1. The peak at the right is caused by *N,N'*-dimethylterephthalamide, which is the product resulting from complete aminolysis of amorphous regions and chain folds of PET. Table I lists the molecular weight distributions of control PET and J-24 after degradation. The polydispersity is close to 1.1, since the PET chains have been reduced to short rods of nearly uniform length.

The results that the molecular weight of control PET and J-24 after methylamine treatment is equal to each other indicates that the fold period of the lamellar crystal reformed during PEG–diamine treatment is the same as that of the original lamellar crystal in control PET. Therefore, it can be confirmed again that the mechanism of changing morphology during PEG–diamine treatment is explained by Schemes 1(A) and 1(D). Conclusively, when PET is aminolyzed with PEG–diamine at 130°C, only amorphous regions are degraded, and simultaneously the amorphous regions are recrystallized so that the fold period of the recrystallized lamella may be the same as that of the lamellar crystal initially present in the biaxially drawn PET film.

Three Different Types of the Lamellar Structure of PET Recrystallized

The PEG chain which is end-capped after PEG–diamine treatment can be incorporated in the crystalline lattice or into the amorphous phase in three different ways as shown in Scheme 2:



Scheme 2. Schematic representation of three different PEG's incorporation structures in PET recrystallized after aminolysis by PEG–diamine. (a) PEG chain is completely excluded out of the crystalline lattice; (b) partially excluded; (c) included in the crystallined lattice; (· · ·) PEG–diamine chain; (——) PET chain.

TABLE I
Molecular Weight and Polydispersity Index of Control PET and J-24 after Aminolysis by 40% Methylamine

Sample code	Aminolysis time (h)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Control	15	2463	2687	1.09
J-24	15	2464	2737	1.11
Control	24	—	—	—
J-24	24	2255	2473	1.10

J-24 sample was aminolyzed with 40% aqueous methylamine solution at room temperature or hydrolyzed with 5*N* aqueous hydrochloric acid solution at 120°C for various lengths of time. Since the ester bonds in the amorphous regions of J-24 are degraded selectively by methylamine treatment, all the PEG chains in the amorphous region will be dissolved out after a critical aminolysis time, but the PEG chains included in the crystalline region or partially excluded from the crystalline lattice with amide bond located at the beginning of the recrystallized lamella can be neither degraded nor dissolved out. All the amide bonds in the amorphous region and at the beginning of the recrystallized lamella can be hydrolyzed by hydrochloric acid, and the hydrolyzed PEG chain can be dissolved out after acid hydrolysis; but any PEG chain included in the recrystallized lamella can be neither hydrolyzed nor dissolved out even after acid hydrolysis.

Figure 8 shows the change in PEG content of J-24 after aminolysis and hydrolysis. The PEG content was rapidly reduced to about 2.2% during 6 h of methylamine treatment, after which the PEG content was constant regardless of aminolysis time. This result indicates that most of the PEG chains (about 74%) are located in the amorphous regions. Acid hydrolysis rapidly reduced the PEG content to about 0.64% within 5 h. After 5 h of acid hydrolysis, the PEG content was hardly changed. Therefore, about 18% of all the PEG chains are partially excluded from the crystalline lattice with the amide bond located

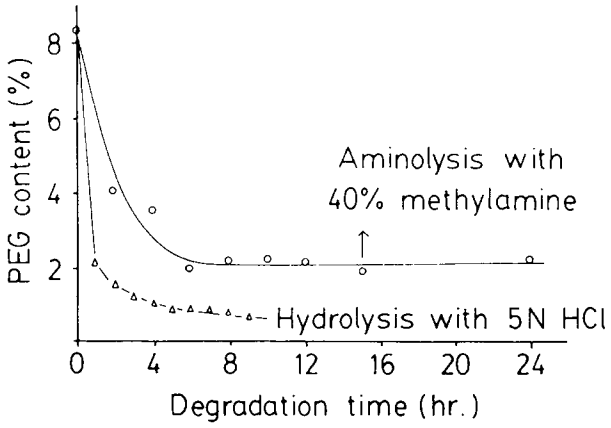


Fig. 8. Change in PEG content of J-24 after aminolysis with 40% methylamine and hydrolysis with 5N HCl.

at the initial point from which the recrystallized lamella begin to grow, while the remainders, i.e., about 8%, are included in the recrystallized lamella.

CONCLUSIONS

The aminolysis of PET by PEG–diamine takes place according to the same chemical reaction as in the aminolysis of PET by alkylamines such as methylamine and ethylamine. The PEG is pseudografted to the PET chain end as a result of the aminolysis of PET by PEG–diamine. Results from measurement of molecular weight, crystallinity, and IR spectra of J-series and from the crystalline fold period measurement after aminolyzing control PET and J-24 sample with methylamine indicate that the selective degradation of amorphous region sand/or the reformation of the chain-folded lamellar crystal with the same fold period as in control PET occur during the aminolysis of PET by PEG–diamine. Most of PEG chains are located in the amorphous regions after aminolysis. Remaining chains are located at the initial point from which the recrystallized lamella begin to grow and are included in the recrystallized lamellar crystal.

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Received January 5, 1988
Accepted May 2, 1988