Thermal Degradation and Cyclodepolymerization of Poly(ethylene terephthalate-*co*-isophthalate)s

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Abstract: The thermal degradation of poly(ethylene terephthalate-*co*-isophthalate)s (PETIs) is investigated by using isothermal thermogravimetric analysis at the temperature range of 280-310°C. The degradation rate of PETIs is increased as the mole ratio of ethylene isophthaloyl (EI) units in PETIs increases. The activation energies for the thermal degradation of poly(ethylene terephthalate), PETI(5/5), and poly(ethylene isophthalate) are 33.4, 16.6, and 8.9 kcal/mole, respectively. The degradation rate of PETIs is influenced by their volatile cyclic oligomer components formed during the polymerization and the thermal degradation. It is simulated by the rotational isomeric state model that the content of cyclic dimer in PETIs, which is the most volatile cyclic oligomer component, increases with the EI units in PETIs.

Keywords: Thermal degradation, Poly(ethylene terephthalate-*co*-isophthalate), Isothermal thermogravimetry, Rotational isomeric state model

Introduction

The thermal degradation of poly(alkylene terephthalate) (PAT), especially poly(ethylene terephthalate) (PET) has been extensively studied from the viewpoints of commercial applications and academic interests[1-10]. It is known that PATs are preferentially degraded through the cleavage of ester bonds between terminal carboxyl and vinyl structures [4,5,9].

PET has various application areas due to its excellent physical and chemical properties. However, various PET copolymers have been also polymerized to improve its processing and performance characteristics[11]. Among them, poly(ethylene terephthalate-*co*-isophthalate)s (PETIs) were developed in the early fifties for modified PET fibers, but less attention has been paid to their thermal degradation behavior occurring at the initial degradation stage. It was reported that 10~15 wt% of the low boiling point liquid components and also the polymer were sublimated during the polymerization of poly(ethylene isophthalate) (PEI), in which cyclic dimer as well as a small amount of cyclic homologs were included[12-14].

Cyclic oligomers of polyesters are normally formed during the polymerization or when heated above their melting temperatures[15-24]. In the case of thermal degradation, most of studies have been focused on the formation of cyclic oligomers of linear aliphatic polyesters rather than aromatic polyesters because their degradation reactions occur more readily. Usually, a different distribution of cyclic oligomers is obtained for each polyester due to the difference of their formation condition.

In this study, the thermal degradation for some of PETIs is studied by using isothermal thermogravimetric analysis (TGA) at the temperature range of 280~310°C under a nitrogen atmosphere, where the thermal degradation would proceed mainly by cyclodepolymerization of PETIs. In addition, to understand the formation of cyclic oligomers during the thermal degradation of PETIs, the molecular dimensions and the molar equilibrium cyclization constants are calculated by using the rotational isomeric state (RIS) model.

Experimental

Polymer Preparation

PETIs were polymerized by the conventional condensation polymerization[14]. A 500 m*l* reactor was charged with a mixture of dimethyl terephthalate and dimethyl isophthalate (50 g, 0.2047 mole) according to the copolymer composition, ethylene glycol (EG)(31.16 g, 0.4094 mole), and calcium acetate(0.055 g, 3.48×10^{-4} mole%) and antimony trioxide (0.0125 g, 4.29×10^{-5} mole%) as catalysts under a dried nitrogen atmosphere. The mixture was then slowly heated to 190°C at atmospheric pressure. Subsequently most of the reaction by-products, methanol, and an excess of EG were removed by distillation. After 3 h, the reaction temperature was raised to 270°C and the pressure of the reaction system was gradually reduced to 1~3 mmHg. The temperature and pressure were maintained for 3.5 h. The inherent viscosity was measured at 25.0± 0.01°C with polymer solution of 0.5 g/d*l* in phenol/1,1,2,2-tetrachloroethane(50/50, v/v).

Extraction of Cyclic Oligomers

Cyclic oligomers in PET, PEI, and PETIs were Soxhlet extracted with 1,4-dioxane or acetone for 24 h. Since the extracts mostly consist of cyclic oligomers, the extracts from

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PET and PEI were designated as CET and CEI, respectively.

Preparation of PET Cyclic Trimer([ET]₃) and PEI Cyclic Dimer([EI]₂)

The Soxhlet extract from PET in 1,4-dioxane was precipitated by adding an excess of water. The precipitant was repeatedly recrystallized in dimethylformamide (DMF) until the pure [ET]₃ was obtained. [EI]₂ was prepared from the recrystallization of the sublimate collected on the wall of the polymerization reactor used for the polymerization of PEI in monochlorobenzene and DMF.

Instrumental Analysis

Isothermal TGA was performed using a du Pont 951 Thermogravimetric Analyzer with a 5~10 mg sample of polymer. For isothermal experiments, samples were heated to a predetermined temperature at a heating rate of 20°C/min and then the temperature was maintained under a nitrogen atmosphere flowing at a rate of 50 ml/min. High-pressure liquid chromatography (HPLC) was performed using a Pye Unicam LC-XP series Liquid Chromatograph equipped with a Technosphere5sil(15 cm×4.6 mm) normal phase column and an ultraviolet detector(wavelength 254 nm) at a flow rate of 1.5 ml/min at 25°C. The solvent was chloroform, and the eluent was hexane/1,4-dioxane(7/3, v/v).

Theoretical Calculations of Molecular Dimensions of PETIs

RIS model was used to determine the molecular dimensions of PETIs[25]. As reported in our previous study, for a relatively simple frame work, alkylene segments were introduced to *m*-phenylene[26,27]. Statistical weight parameters were used as the same values for PET determined by Flory, i.e., $\sigma_k = 0.5$, $\sigma_\eta = 1.5$, and $\omega_{\eta k} = 0.1$.

Results and Discussion

Table 1 shows inherent viscosities of PETIs used in this study. Usually, the inherent viscosity is dependent on the chemical structure of polymer and chain conformation in

Table 1. Inherent viscosities of PET, PETIs, and PEI

| PETI (ET/EI)	Inherent viscosity (dl/g)
100/0	0.51
90/10	0.48
80/20	0.47
70/30	0.50
60/40	0.46
50/50	0.45
40/60	0.51
30/70	0.51
20/80	0.54
10/90	0.48
0/100	0.48

solution. Although they show some deviation, it is assumed that the effect of molecular weight on the thermal degradation of PETIs is negligible. It is generally accepted that a copolyester prepared by condensation polymerization or by melt blend has the random distribution of their structural units due to trans-esterification. Ha *et al.*[28] obtained a completely random PETI copolymer from a PET/PEI(6/4, w/w) blend by using a mini-max molder at 270°C for 30 min. Therefore, PETIs prepared by condensation polymerization in this study are regarded to have the random sequence distribution.

Both isothermal and dynamic TGA have been widely used to determine kinetic parameters for polymer decomposition such as activation energy, pre-exponential factor, and reaction order[29]. Dynamic TGA can identify different reaction stages in the solid-gas system from a single scan with the same sample, but they are subject to serious errors in analyzing the data. In the case of isothermal TGA, though several experiments at various isothermal temperatures should be carried out to obtain those kinetic parameters, the calculation of kinetic parameters is less cumbersome in comparison with dynamic TGA. Therefore, isothermal TGA is employed in this study to evaluate the thermal degradation of PETIs. Apparent activation energies of isothermal degradation can be determined from the Arrhenius relationship:

$$k = dW/dt = A\,W^n\exp(-E_a/RT) \tag{1}$$

where, k is the degradation rate (%/min), W is the weight of the remaining sample, n is the order of reaction, t is the degradation time, A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant.

Figure 1 shows the isothermal TGA curves of PET, PETI (5/5), and PEI at 300°C under a nitrogen atmosphere. Although the degradation rate data are not consistent at the very early stage, all the curves show a linear relationship after 20 min. The degradation rates are determined from the
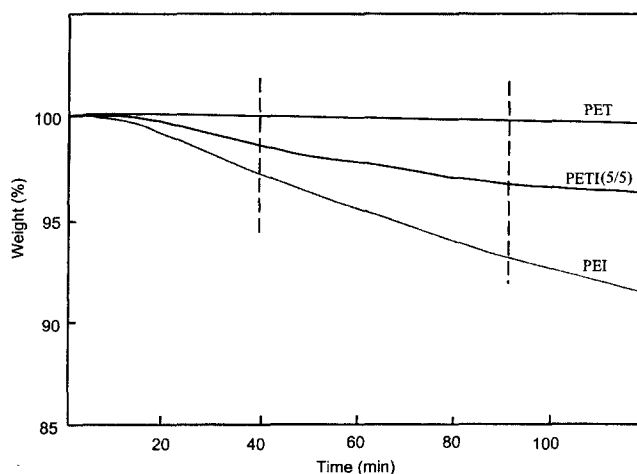
Figure 1. Isothermal TGA curves of PET, PETI(5/5), and PEI at 300°C.

linear weight loss slopes for the time range of 40~90 min. We disregarded the data obtained at the very early stage because there is some fluctuation of temperature as a result of heating. Linear slope at the isothermal condition means that the degradation occurs according to the zero order kinetics. Taking n zero onto a logarithm of equation (1), E_a is obtained from the slope of the plot of ln k against $1/T$.

The Arrhenius plot of PET free of cyclic oligomer is shown in Figure 2. The activation energy for the degradation of PET is 33.4 kcal/mole. This is in good accordance with the results reported by other researchers[8 and therein]. The almost same activation energy is obtained for PET free of cyclic oligomers, indicating that cyclic oligomers in PET do not affect the activation energy of the degradation. Usually, a commercial PET contains 1~2 wt% of cyclic oligomers as an equilibrium product[30-32]. Also, the sublimate formed during the polymerization of PET is much smaller in amount and much less volatile than that isolated from PEI polymerization[12]. McNeill and Bounekhel reported that only a small amount of [ET]$_3$ was obtained in the sublimate of PET maintained at 305°C for 100 min[9].

Figure 3 shows the change of thermal degradation rates of PETIs at 300°C. The degradation rate is increased with the content of ethylene isophthaloyl (EI) units in PETIs. Activation energies for the thermal degradation of PETI(5/5) and PEI are 16.6 and 8.9 kcal/mole, respectively. The activation energies are dependent on the content of m-phenylene units in PETIs because the molar thermal decomposition function ($Y_{d,1/2}$) of m-phenylene unit(44~65 K·kg/mole) is lower than

that of p-phenylene unit(54~75 K·kg/mole)[33]. The molar thermal decomposition function has a linear relationship with the characteristic decomposition temperature($T_{d,1/2}$) and the activation energy of decomposition. Higher activation energies are obtained from PETI(5/5) and PEI after extraction of their cyclic oligomers with acetone. 2.8 wt% and 5.3 wt% of cyclic oligomers are extracted from PETI(5/5) and PEI,
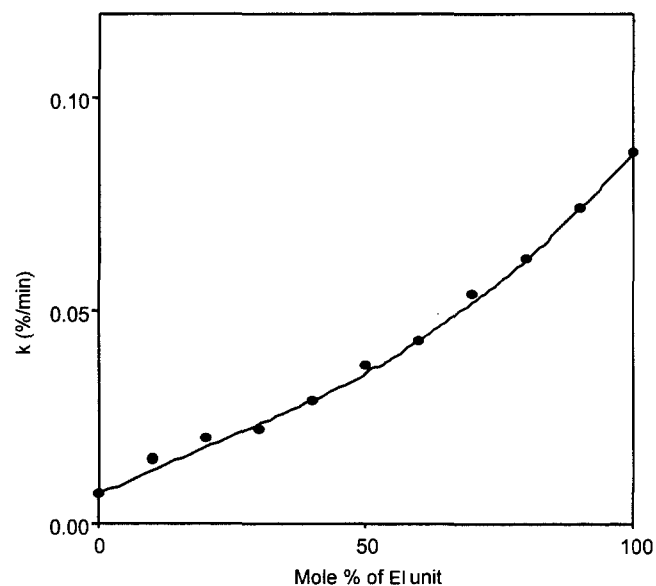

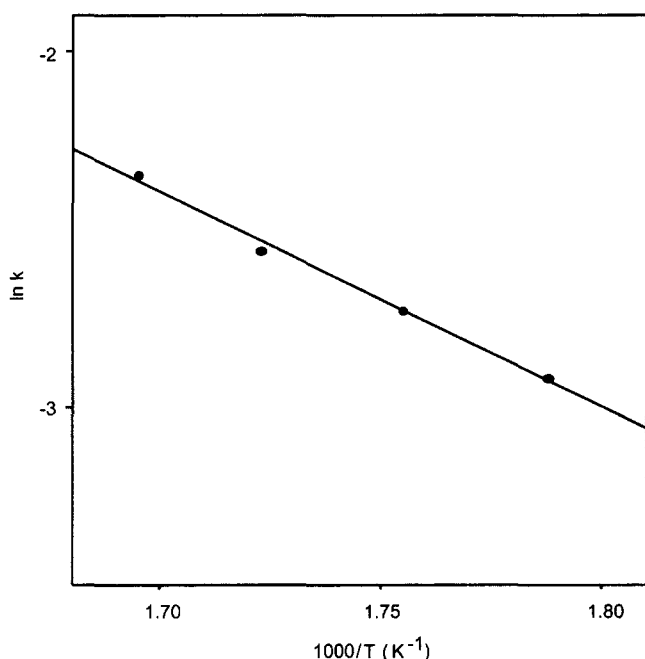**Figure 3.** Thermal degradation rates of PET, PETIs, and PEI at 300°C.

Figure 2. Arrhenius plot of the thermal degradation for PET free of cyclic oligomers.
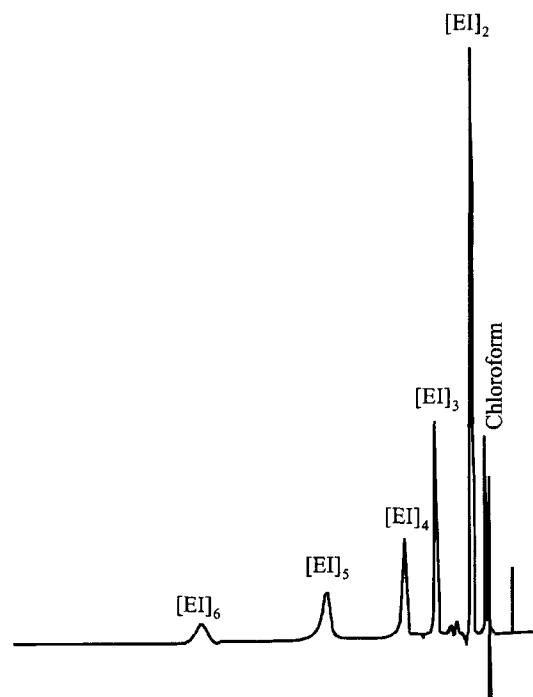

Figure 4. HPLC curve of CEI.

respectively. It can be postulated that a polymer sample containing cyclic oligomers, which are readily formed and volatile, has lower activation energy than the sample free of cyclic oligomers. As shown in Table 2, the increase of degradation rate for the polymer samples free of cyclic oligomers confirms this assumption.

Isothermal TGA data for CET and CEI at 300°C in Table 3 also indicate their higher degradation rate or volatility than those of PET and PEI. HPLC curve of Figure 4 shows that CEI consists mostly of [EI]$_2$. Assuming that cyclic oligomers have the same detector response per unit repeating unit, the content of [EI]$_2$ in CEI determined from HPLC peak is *ca.* 73%. Also, all cyclic oligomers have higher initial degradation rates than the corresponding polymers and a cyclic oligomer component has higher degradation rate than the homologs of higher molecular weight. For example, [EI]$_2$ is readily sublimated than CEI as shown in Table 3. Also [EI]$_2$ has higher rate constant than [ET]$_3$. The degradation rate is closely related to the amount of cyclic oligomers formed at the polymerization and at the thermal degradation stage as well.

The ester linkages are mainly cleaved to vinyl ester and carboxyl groups during the thermal degradation of PET. This reaction is accompanied by the intramolecular cyclization. Montaudo *et al.*[33-35] obtained aromatic cyclic oligomers by thermal decomposition of aromatic polyesters. In the thermal degradation of polycarbonates, cyclic oligomers were generated by an intramolecular exchange reaction[35, 36]. It is generally accepted that polymers having reactive functional group in the backbone and chain end are capable of undergoing exchange reactions during the thermal degradation.

Goodman and Nesbitt suggested for the first time that the

Table 2. Thermal degradation activation energies and degradation rates at 300°C for PET, PETI(5/5), PEI

Polymer	E_a (kcal/mole)	k (%/min)
PET	33.4	0.0042
PETI(5/5)	16.6	0.0074
PEI	8.9	0.0144
PET[a]	32.8	0.0468
PETI(5/5)[b]	22.9	0.0079
PEI[b]	11.3	0.0139

[a] Extracted with 1,4-dioxane, [b] Extracted with acetone.

**Table 3.** Thermal degradation rates of some cyclic oligomer component(s) at 300°C

Cyclic oligomer component(s)	k (%/min)
CET	0.036
CEI	0.661
[ET]$_3$	0.030
[EI]$_2$	0.821

cyclization of PET can occur *via* three different routes [37,38]. Ha and Choun confirmed that intramolecular transesterification by hydroxyl chain end is the main route among the proposed ones[39]. In this case, the cyclization probability is directly related to the end-to-end distances of the corresponding linear oligomers as predicated by Jacobson-Stockmayer as follows[40]:

$$K_x = (3/2\pi \cdot <r_x^2>_o)^{3/2} (1/2\sigma_{Rx} \cdot N_A) \qquad (2)$$

where K_x is the molar cyclization equilibrium constant, $<r_x^2>_o$ represents the statistical mean square values of the end-to-end distances of the corresponding x-meric open chain molecules, σ_{Rx} is a symmetry number, and N_A is the Avogadro constant. The equilibrium concentration of each cyclic oligomer component in this study is proportional to $n^{-2.5}$, where n is the ring size, that is, the number of repeating units in a ring. This indicates that the thermal degradation of PETIs is controlled thermodynamically. It was reported that the distribution of cyclic oligomers formed during the thermal degradation of aliphatic polyesters, polyamides, and polycarbonates decreases in proportional to $n^{-2/5}$(thermodynamically controlled process)[22,23]. However, the distributions of cyclic oligomers obtained from the thermal degradation of polycaprolactone, poly(lactide acid), and poly(glycolic acid) were decreased with $n^{-1.5}$ because they were controlled kinetically[23].

In our previous study, the molecular dimensions of PEI and PETIs were calculated by using the RIS model[27]. New description for aromatic segments was introduced and the statistical weight parameters of PET were adopted. In the case of random copolymers, the mean-square dimension
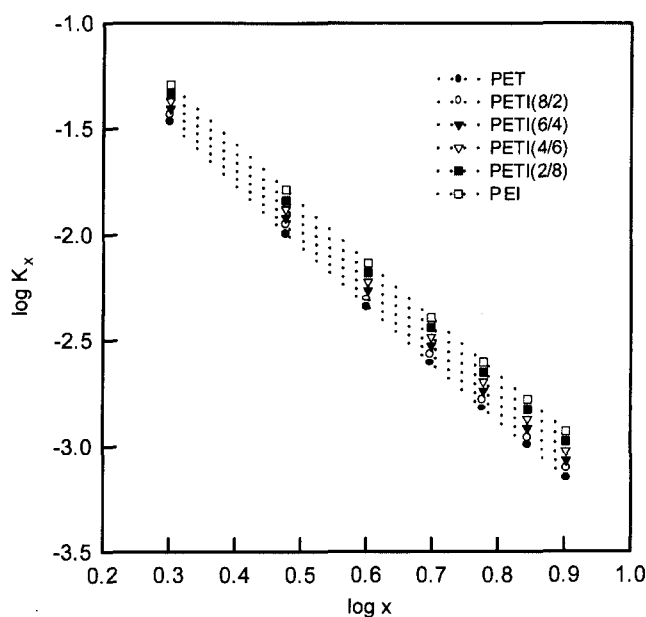
Figure 5. Molar cyclization equilibrium constants of PET, some PETIs, and PEI.

ratio($(<r^2>_0/M)$) may be calculated by[25]:

$$\overline{G} = w_a G_a + w_b G_b \tag{3}$$

where w_a and w_b are the mole fractions of units a and b and G_a and G_b are matrixes containing all thermodynamic and geometrical information for units a and b, respectively. The mean-square dimension ratios of PEI and PET are 0.653 and 0.933, respectively[25,27]. The mean-square dimension ratio of PETI calculated is decreased almost linearly according to the increase of EI units from 0.933 to 0.635.

Figure 5 shows the molar equilibrium cyclization constants of PETIs calculated with equation (2) using the end-to-end distances of corresponding linear oligomers. As expected, these constants are increased with increasing the mole ratio of EI units. This result is also confirmed by the fact that the amount of cyclic oligomers extracted from copolymers increases with the content of EI units in PETIs[14].

The content of cyclic oligomers(W_x) formed in PETIs is calculated from the following equation[41]:

$$W_x = M_x \cdot K_x / 10 \cdot \rho \tag{4}$$

where M_x is MW of cyclic x-mer and ρ is the density of polymer. In this study, the density of PET 1.16 g/mole was applied to other densities of PETIs and PEI. Figure 6 shows the calculated contents of cyclic dimer formed in PET, PETIs, and PEI. In the case of PET, 1.1 wt% of cyclic dimer is theoretically calculated but it is barely detected experimentally[32]. From Figure 6, it can be noticed that the incorporation of EI units into PET facilitates the formation of cyclic dimer. The content of [EI]$_2$, which is the most
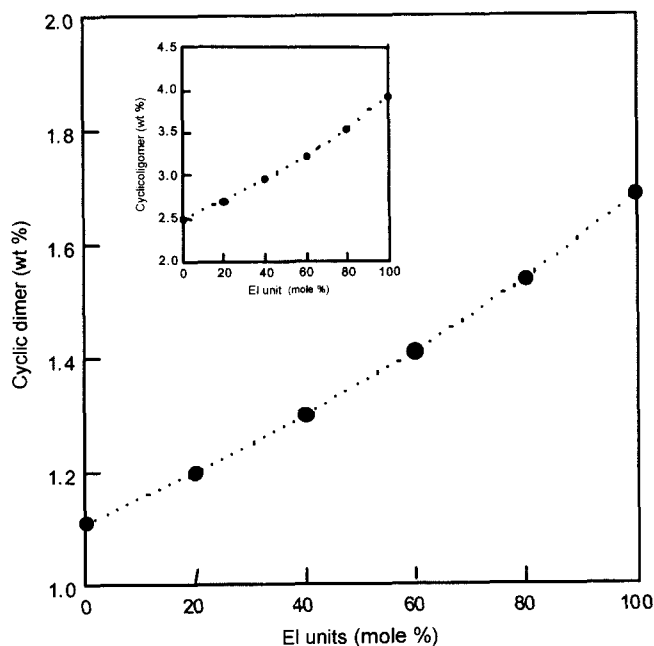
Figure 6. The contents of cyclic dimer and oligomers calculated in PET, PETIs, and PEI.

volatile one, increases with the content of EI units in PETI. Therefore, it is considered that this result is closely related to the thermal degradation rate of PETIs.

Conclusion

The thermal degradation of PETIs is investigated by using isothermal thermogravimetric analysis at the temperature range of 280-310°C. The degradation rate of PETIs is increased as the mole ratio of EI units in PETIs increases. Higher activation energies are obtained from PETI(5/5) and PEI after extraction of their cyclic oligomers with acetone. It is found that the degradation rate of PETIs is influenced by the volatile cyclic oligomer components formed during the polymerization and the thermal degradation. Simulation by the rotational isomeric state model shows that the mean-square dimension ratio of PETI calculated is decreased almost linearly according to the increase of EI units from 0.933 for PET to 0.635 for PEI, and the incorporation of EI units into PET facilitates the formation of cyclic dimer.

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