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Molecular dimensions of poly(ethylene isophthalate) and poly(ethylene naphthalene-2,6-dicarboxylate)

Ji Ho Youk[1], **Won Ho Jo**[1,*], **Dong Il Yoo**[2]

[1] Department of Fiber and Polymer Science, Seoul National University,
Seoul 151-742, Korea
[2] Department of Textile Engineering, College of Engineering, Chonnam National University,
Kwangju 500-757, Korea

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Summary

The rotational isomeric state (RIS) model was used to calculate the molecular dimensions of poly(ethylene isophthalate) (PEI) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) by introducing new description for aromatic segments and by adopting the statistical weight parameters of PET. The mean square dimension ratios ($(\langle r^2\rangle_0/M)_\infty$) of PEN and PEI were 0.653 and 1.167, respectively, and the entanglement molecular weight (M_e) of PEI and PEN were 1850 and 1810, respectively.

Introduction

The conformational state of polymers can often be expressed by their unperturbed dimensions.[1] The unperturbed dimension of polymers represented by the value of K_θ is indirectly determined from the Stockmayer-Fixman extrapolation equation[2] for the solution viscosity. Several researchers[3-6] measured the value of K_θ for poly(ethylene terephthalate) (PET) to analyze its conformational state. However, few works have been reported on the unperturbed dimensions of poly(ethylene isophthalate) (PEI) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN). The chain rigidity of such polyesters is strongly dependent upon the difference of aromatic structure.

Flory and Williams[7] assumed the average K_θ value of PET to be in the range of $2.8 \sim 3.0 \times 10^{-3}$ $d\ell$ $g^{-3/2}$ $mol^{1/2}$ and then determined its statistical weight parameters from the best fit of the value of K_θ to the value determined experimentally. Also, Semlyen et al.[8-10] used the concentration of cyclic oligomers and its distribution in PET melt equilibrate to determine the statistical weight parameters of PET.

In this study, the molecular dimensions of PEI and PEN are determined by the RIS model. In applying the RIS model to the systems, we use the statistical weight parameters of PET determined by Flory and Williams.[7]

Theory and model descriptions

Description of the polyester chain. The unperturbed dimensions of linear polymers have now been successfully correlated with their chain structures and the hindrance to bond rotation. The RIS model[11] has very often been used to calculate the molecular dimension

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* Corresponding author

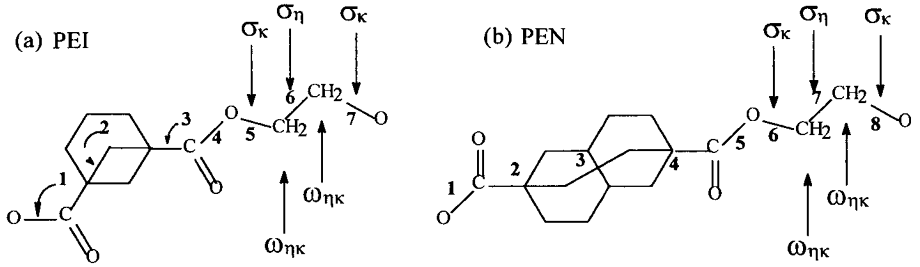

Fig 1. The definition of virtual and real bonds in a repeating unit of PET and PEN. The statistical weights of the first order (σ_i) and the second order (ω_{ij}) are indicated.

of polymers. Generally, a rigid aromatic moiety is often replaced by a single virtual bond when the RIS model is applied to polymers containing aromatic moieties. However, *m*-phenylene and naphthalene moieties in PET and PEN do not exhibit collinear exocyclic chain continuation bonds. Thus, in order to fit within a relatively simple framework, the oxygen-the carbonyl carbon in the proceeding ester is defined as the first bond and the carbonyl carbon-the geometric center of the ring in *m*-phenylene unit of PEI is defined as the second bond as shown in Figure 1(a). The third bond in the PEI repeat unit extends from the center of the ring to the carbonyl carbon of the succeeding ester group. In the PEN, the third bond defines the virtual bond connecting the centers of the first ring and the second ring, and the fourth bond extends from the center of the second ring to the carbonyl carbon in the succeeding ester group. The definitions of virtual bonds of PEI and PEN are shown in Figure 1. The bond angle θ_i is defined as the angle between bonds i and i+1. Bond lengths and bond angles of PEI and PEN are listed in Table 1.

Table 1. Structural parameters for PEI

Polymer	Bond length (Å)	Bond angles (degree)
PEI	$\ell_{O\text{-}CO} = \ell_1 = \ell_4 = 1.34$	$\theta_1 = \theta_3 = 66$
	$\ell_2 = \ell_3 = 2.88$	$\theta_2 = 60$
	$\ell_{O\text{-}C} = \ell_5 = \ell_7 = 1.44$	$\theta_4 = \theta_7 = 67$
	$\ell_{C\text{-}C} = \ell_6 = 1.53$	$\theta_5 = \theta_6 = 70$
PEN	$\ell_{O\text{-}CO} = \ell_1 = \ell_5 = 1.34$	$\theta_1 = \theta_4 = 66$
	$\ell_2 = \ell_4 = 2.88$	$\theta_2 = \theta_3 = 30$
	$\ell_3 = 2.41$	$\theta_5 = \theta_8 = 68$
	$\ell_{O\text{-}C} = \ell_6 = \ell_8 = 1.44$	$\theta_6 = \theta_7 = 70$
	$\ell_{C\text{-}C} = \ell_7 = 1.53$	

Assignment of statistical weight parameters. The statistical weight of *trans* conformation is assigned as unity, and σ and ω represent statistical weight factors for the first-order interaction (three bond interaction) and the second-order interaction (four bond interaction), respectively.

At the first glance, the ester group seems to have the *trans* state because of the double-bond character of the ester group. However, Flory[7] assumed that the *cis* and *trans* conformations were about equally probable. In fact, two equal energy minima were observed,[12,13] when the carbonyl carbon was bonded directly to the ring. In this study, we also assume that the torsional angle of the bond of carbonyl carbon to the ring is equally probable for 0° and 180°. In PEN, the bond 3 is restricted to the *trans*. The other statistical bonds of the repeat unit are restricted to one of three rotational states, i.e., *trans*, *gauch* positive and *gauch* negative, and the values for PET determined by Flory and williams,[7] i.e., σ_k=0.5, σ_η=1.5, and $\omega_{\eta k}$=0.1, were used as the statistical weight parameters of PEI and PEN.

Theoretical calculations. The conformational partition function for the *k*th independent repeat unit of chains is expressed as follows:[11]

$$Z_k=\mathbf{U}_1\mathbf{U}_2 \cdot \cdot \cdot \mathbf{U}_\xi \mathbf{J} \qquad (1)$$

where $\mathbf{U}_i$ is the statistical weight matrix for the *i*th bond in the *k*th repeat unit, and **J** extracts desired terms from the matrix product. The subscript ξ corresponds to the number of statistical skeletal bonds in a repeat unit of the chain. The mean square end-to-end distance may be written as:

$$<r^2>=2\mathbf{I}^*(\mathbf{G}^{(\xi)})^x\mathbf{I} \qquad (2)$$

where the superscript x is the degree of polymerization and $\mathbf{I}^*$ is the row vector consisting of a single unity followed by four zeros, **I** is the column vector consisting of four zeros followed by a single unity, and $\mathbf{G}^{(\xi)}$ is given by

$$\mathbf{G}^{(\xi)}=\mathbf{g}_k^{(\xi)}\begin{pmatrix}\mathbf{J} & 0 & 0\\ 0 & \mathbf{J}\otimes\mathbf{E} & 0\\ 0 & 0 & \mathbf{J}\end{pmatrix}(\mathbf{Z}_k)^{-1} \qquad (3)$$

$$\mathbf{g}_k^{(\xi)}=\mathbf{g}_1\mathbf{g}_2 \cdot \cdot \cdot \mathbf{g}_\xi \qquad (4)$$

where $\mathbf{g}_i$ is the generator matrix that contains all thermodynamic and geometrical parameters relating to bond I, and $\mathbf{J}\otimes\mathbf{E}$ is the Kronecker product of matrices **J** and **E**.[11]

In the case of random copolymer, the unperturbed dimension may be calculated by:

$$\overline{\mathbf{G}} = w_a\mathbf{G}_a + w_b\mathbf{G}_b \qquad (5)$$

where w_a and w_b are the mole fraction of units a and b and $\mathbf{G}_a$ and $\mathbf{G}_b$ are serial product of eq. 3 of units a and b, respectively.

Results and Discussion

Values of $<r^2>_0/M$ of PEI, PET, PEN and their copolymers are plotted against the number of repeat units in Figure 2. The value of $<r^2>_0/M$ rapidly converges to an asymptotic value as the number of repeat units increases. The values of $<r^2>_0/M$ of PEI and PEN in the limit of $M=\infty$ are 0.653 and 1.167 $Å^2$ mol g^{-1}, respectively. These values lead to calculate the values of K_θ for PEI and PEN from the following equation:

$$K_\theta = \Phi_0(<r^2>_0/M)^{3/2} \qquad (6)$$

where Φ_0 is the universal constant of 2.6×10^{23}. The calculated K_θ value of PEI and PEN were 1.4×10^{-3} and 3.3×10^{-3} $d\ell\ g^{-3/2}\ mol^{1/2}$, respectively. As can be expected from the bending characteristic, the K_θ value of PEI is lower than that of PET[7] ($2.8\sim3.0\times10^{-3}$ $d\ell\ g^{-3/2}\ mol^{1/2}$). Each isophthaloyl group of PEI gives a 60° bending to the direction of polymer chain. This disturbs the straight zig-zag structure of chains, resulting in the steric hindrance of an optimum chain arrangement. Aharoni[14] experimentally measured the K_θ value for PEI by use of the Stockmayer-Fixmann equation. The experimentally determined value (2.0×10^{-3} $d\ell\ g^{-3/2}\ mol^{1/2}$) is somewhat larger than the calculated value in this study.

On the other hand, PEN has a higher value of $<r^2>_0/M$ than that of PET. The naphthalene ring of PEN imparts higher stiffness to the polymer backbone than the benzene ring of PET, leading to improved thermal resistance, excellent mechanical properties, and outstanding gas barrier characteristic.[15,16]

The characteristic ratio (C_∞) and the entanglement molecular weight (M_e) are two important parameters relating to melt viscoelasticity, solid mechanical behavior, and adhesion of polymers. The C_∞ in the limit of long chains is defined as follows:

$$C_\infty = (K_\theta / \phi_0)^{2/3} M_b / \ell^2 \qquad (7)$$

where M_b is the mean molecular weight per skeletal bond and ℓ is the mean bond length. Usually, the M_e is determined from the plateau modulus by[17]:

$$M_e = \rho RT/G^0_N \qquad (8)$$

where ρ is the melt density at temperature T, R the gas constant and G^0_N the plateau modulus. In polymer melt, the value of C_∞ is determined by the intrinsic stiffness of polymer chain. Wu[18] has shown that the entanglement molecular weight can be expressed as follows:

$$M_e = 3M_vC_\infty^2 \qquad (9)$$

$$M_v = M_r/n_v \qquad (10)$$

where M_v is the average molecular weight per statistical skeletal unit, M_r the molecular

Table 2. Calculated characteristic parameters of PET, PEI, and PEN

Polymer	$(\langle r^2\rangle_0/M)_\infty$ ($Å^2 g^{-1} mol$)	$K_\theta(\times 10^3)$ ($d\ell\, g^{-3/2}\, mol^{1/2}$)	C_∞	M_e (g/mol)	$\langle r_c\rangle$ (Å)
PET	0.933	2.3	4.70	2120	62.90
PEI	0.653	1.4	4.74	1850	49.15
PEN	1.167	3.3	3.87	1810	65.00

weight of a repeat unit, and n_v the number of statistical skeletal units in a repeat unit. The critical end-to-end distance for entanglements, $\langle r_c\rangle$, has been calculated from the critical molecular weight M_c through the following relation:[11]

$$\langle r_c\rangle = \langle r_c^2\rangle^{1/2} = M_c^{1/2}(\langle r^2\rangle_0/M)^{1/2} \qquad (11)$$

When the M_c and M_e values of the same polymers are compared, the ratio M_c/M_e is estimated by about 2.[19,20] A statistical skeletal unit is a real or a virtual skeletal bond, which is an elementary rotational unit on the main chain. The value of C_∞ has some ambiguity owing to the method of definition of bonds or virtual bonds. A repeat unit of PET consists of a virtual bond CO-ϕ-OC (ℓ =5.74 Å) and five other real bonds, CO-O, O-CH_2, CH_2-CH_2, CH_2-O, and O-CO. A repeating unit of PEI is composed of two CO-ϕ (2.88 Å) bonds and five other skeletal bonds, like PET. The PEN comprises of a rigid segment extending from one carbonyl to the other of a naphthaloyl residue (7.93 Å) and five other skeletal bonds. The calculated mean square dimension ratio, characteristic ratio, critical end-to-end distance for entanglements, and entanglement molecular weight of three polyesters are listed in Table 2. The calculated value of C_∞ for PET, PEI, and PEN were 4.70, 4.74, and 3.78, respectively. The values of C_∞ for PET and PEI were collected from literatures and listed in Table 3. When the calculated values of C_∞ for PET and PEI in Table 2 are compared with the experimental values listed in Table 3, the calculated values are in good agreement with the experimental ones.

Table 3. Characteristic ratio of PET and PEI

Polymer	C_∞	M_e (g / mol)	Reference
PET	4.20	1450	4
	3.50	1180	6
	4.21	1600	14
	3.56	1210	21, 22
	5.83	1635	24
PEI	4.29	4750	14
	7.75	4950	21, 22

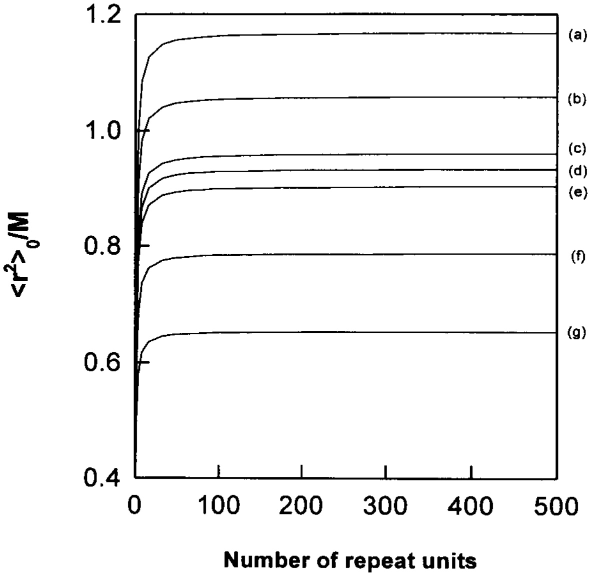

Fig. 2. The mean-sqare dimension ratio calculated as a function of chain length.: (a) PEN, (b) PET/EN (50/50), (c) PET/EN (90/10), (d) PET, (e) PET/EI (90/10), (f) PET/EI (50/50), (g) PEI.

The calculated values of C_∞ for PET and PEI in Table 2 are in good agreement with the experimental values listed in Table 3. The competition between shear yielding and crazing in fracture and deformation of polymers determines the brittle-ductile behavior. Polymers having $C_\infty > \sim 7.5$ tend to craze and are brittle whereas polymers having $C_\infty < \sim 7.5$ tend to yield and are intrinsically ductile.[21,22] Therefore, all of three polyesters may be classified as ductile polymers.

Modified PET fibers play an important role commercially because they exhibit improved processing and performance characteristics compared with conventional PET fibers. The modification of PET by incorporation of isophthalic acid unit had already been developed in the early fifties. Recently, the modification of PET with 2,6-naphthalene dicarboxylic acid or the modification of PEN with terephthalic acid has received much attention. In copolyesters, it is expected that the unperturbed dimension of PET changes with the fraction of isophthalic acid or 2,6-naphthalene dicarboxylic acid. Figure 2 shows the unperturbed dimensions of PET/EI and PET/EN random copolymers with various mole ratios. It is reported that the melt viscosity of the copolymer melt does not practically change with the copolymer composition up to an isophthaloyl group content of 15 mole%. However, unlike the previous study,[23] the calculated unperturbed dimension of random copolyesters is almost linearly proportional to the mole ratio of comonomer unit.

Conclusions

The mean square dimension ratios ($\langle r^2\rangle_0/M_\infty$) of PEI and PEN were calculated by the RIS model. In applying the RIS model to PEI and PEN, the statistical weight of PET were used. The values of PEI and PEN were 0.635 and 1.167 Å^2 mol g^{-1}, and the molecular weight of entanglement were 1850 and 1810, respectively. The characteristic ratios of PEI and PEN were also calculated. The values were relatively low, indicating that these polyesters are intrinsically ductile. In random copolyesters, the molecular dimension of PET/PEI or PET/PEN was linearly proportional to the mole fraction of comonomer unit.

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