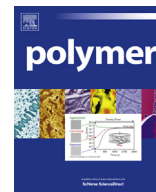




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Conformational characteristics and configurational properties of poly(butylene terephthalate) and structure–property relationships of aromatic polyesters

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ABSTRACT

Conformational analysis of poly(butylene terephthalate) (PBT) has been carried out by the refined rotational isomeric state scheme combined with *ab initio* molecular orbital (MO) calculations and NMR experiments on its model compound, tetramethylene glycol dibenzoate (TetMGDB). Two conformers of TetMGDB, showing intramolecular phenyl–phenyl close contacts, yielded so small free energies at the MP2 level that the overestimated MP2 stabilization for the π – π attraction was compensated by addition of the hemi-MP3 term. The altered MO energies satisfactorily reproduced the NMR and dipole moment data on TetMGDB. The energy correction was also applied to poly(trimethylene terephthalate) (PTT), and configurational properties of PBT and PTT were evaluated from the altered energies. Fluorescence emissions observed from poly(ethylene terephthalate) (PET), PTT, PBT, and their model compounds were well correlated with the spacer conformations. Configurational, thermal, and optical properties of the aromatic polyesters of industrial importance are discussed herein in terms of their conformational characteristics.

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1. Introduction

The aromatic polyesters expressed as $[-\text{OCC}_6\text{H}_4\text{COO}(\text{CH}_2)_y\text{O}-]_x-$ have been mass-produced and used in a variety of materials for industries and our daily lives. Poly(ethylene terephthalate) (PET, $y = 2$) is so rigid as to be molded into fiber, films, and bottles, poly(trimethylene terephthalate) (PTT, $y = 3$) is rather elastic and used in, e.g., sportswear and innerwear, and poly(butylene terephthalate) (PBT, $y = 4$, Fig. 1) is so superior in impact resistance as to be adopted in automotive and electric parts [1].

In previous studies [2,3], we investigated conformational characteristics of PET and PTT by means of *ab initio* statistical mechanics, viz., the refined rotational isomeric state (RIS) scheme [4–6] combined with *ab initio* molecular orbital (MO) calculations. The present study has dealt with PBT for comprehensive elucidation of structure–property relationships of the aromatic polyesters. In this paper, the conformational analysis of PBT is described first. In the analysis, intramolecular π – π interaction energies between benzene rings, evaluated at the MP2 level, were modified. The energy correction was

also applied to PTT, and the results are reported herein. In addition, fluorescence emissions of the three polyesters are interpreted in terms of conformations of their spacers ($-\text{O}(\text{CH}_2)_y\text{O}-$).

2. Methods

2.1. MO calculations on model compounds

Density functional and *ab initio* MO calculations were carried out with the Gaussian09 program [7] installed on an HPC Systems 5000-Z800 computer or a HITACHI SR16000 computer in the Institute of Media and Information Technology of Chiba University. For each conformer of tetramethylene glycol dibenzoate (TetMGDB, Fig. 1b), the geometrical parameters were fully optimized at the B3LYP/6-311++G(2df,2p) level, and the thermal-correction term to the Gibbs free energy (at 25 °C), dipole moments, and polarizabilities were calculated at the same level. Bond lengths, bond angles, and dihedral angles used in the refined RIS computations for PBT were chosen from the optimized geometrical parameters (see Table S5, Supplementary data). All self-consistent field (SCF) calculations were conducted under the tight convergence. With the optimized geometry, the single point energy (EUMP2) calculation was performed at the MP2/6-311++G(2df,2p) level. The Gibbs free energy was

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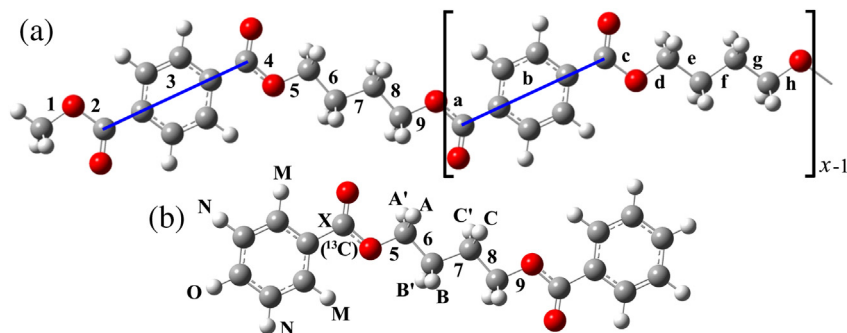


Fig. 1. All-trans states of (a) poly(butylene terephthalate) (PBT) and (b) tetramethylene glycol dibenzoate (TetMGDB). The thick line segment expresses the virtual bond of the aromatic ring. The bonds are labeled as indicated. The hydrogen and carbon atoms of TetMGDB are partly designated to represent the NMR spin system.

evaluated from the EUMP2 and thermal correction energies, being given here as the difference from that of the all-trans conformer and denoted as ΔG_k (k : conformer). Vicinal ^1H – ^1H and ^{13}C – ^1H coupling constants of TetMGDB for NMR analyses were calculated at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level [8]. The ΔG_k values for a benzene medium at 25 °C were also calculated at the MP2/6-311++G(2df,2p) level with the integral equation formalism of the polarizable continuum model [9].

For the sake of compliance with previous studies, the dihedral angle is defined here according to the tradition in polymer science [4]: trans (t) $\sim \pm 0^\circ$; cis (c) $\sim \pm 180^\circ$; gauche⁺ (g⁺) $\sim +120^\circ$; gauche[−] (g[−]) $\sim -120^\circ$. Some non-SI units are used: free energy in kcal mol^{−1} (1 kcal mol^{−1} = 4.184 kJ mol^{−1}); dipole moment in D (1 D = 3.3356 × 10^{−30} C m); bond length in Å (1 Å = 10^{−10} m).

2.2. Synthesis of TetMGDB

Benzoyl chloride (4.1 mL, 35 mmol) was added through a dropping funnel to 1,4-butanediol (1.48 mL, 17 mmol) and pyridine (2.8 mL, 35 mmol) stirred by a mechanical stirrer in a three-necked flask bathed in ice water, and then the mixture was stirred at room temperature for 28 h. The reaction mixture underwent extraction with diethyl ether and distilled water. The organic layer was washed three times with 10% aqueous sodium bicarbonate (30 mL), dried overnight over anhydrous magnesium sulfate, and filtrated. White solidified product was recrystallized from methanol to yield TetMGDB.

2.3. Synthesis of tetramethylene glycol dibenzoate-¹³C₁ (TetMGDB-C₁)

Benzoyl chloride (26.5 mL, 0.23 mol) was added dropwise to 1,4-butanediol (31 mL, 0.35 mol) and pyridine (18.5 mL, 0.23 mmol) stirred and cooled as described above, and then the mixture was stirred at room temperature for 12 h. The reaction mixture underwent extraction with diethyl ether (50 mL) and water (50 mL). The ether layer was washed and dried as above, and then distilled under reduced pressure (5 mmHg, 151 °C) to yield tetramethylene glycol monobenzoate.

Benzoyl-carbonyl-¹³C chloride (Isotec, 99 atom% ¹³C, 0.5 g) was added through a syringe to tetramethylene glycol monobenzoate (0.89 g, 4.6 mmol) and pyridine (0.28 mL, 3.5 mmol) stirred and cooled as above, and then the reaction mixture was stirred at room temperature for 12 h and subjected to extraction, washing, drying, and filtration as described above. The collected white solid was recrystallized from methanol to yield TetMGDB-C₁.

2.4. NMR measurements

Proton (¹³C) NMR spectra were recorded at 500 MHz (126 MHz) on a JEOL JNM-ECA500 spectrometer equipped with a variable temperature controller in the Chemical Analysis Center of Chiba University. The measurement temperatures were 15, 25, 35, 45, and 55 °C and maintained within ± 0.1 °C fluctuations. Pulse induction decays were accumulated 32 (256) times. The $\pi/2$ free width, data acquisition time, and recycle delay were 5.7 (3.3) μs , 7.0 (2.1) s, and 2.0 (2.0) s, respectively. In the ¹³C NMR experiments, the gated decoupling technique was employed under the

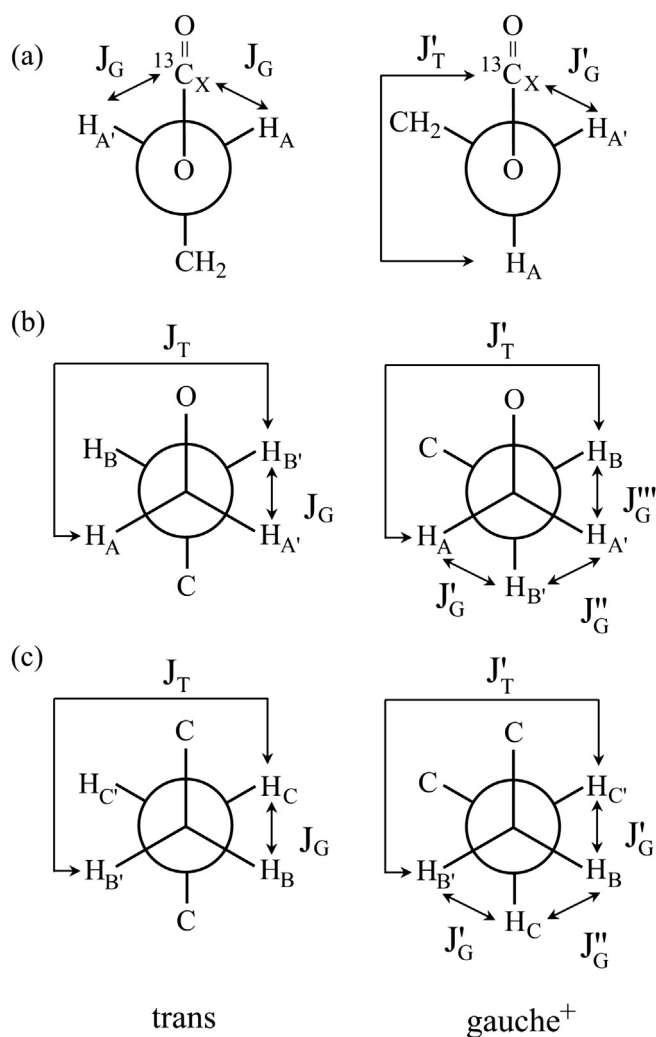


Fig. 2. Rotational isomeric states around (a) O–CH₂, (b) OCH₂–CH₂, and (c) CH₂CH₂–CH₂CH₂ bonds of TetMGDB and PBT with definitions of vicinal trans (J_T) and gauche (J_G) coupling constants.

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