Structure—Property Relationships of Poly(ethylene carbonate) and Poly(propylene carbonate)

Yuji Sasanuma* and Yuta Takahashi

Department of Applied Chemistry and Biotechnology, Graduate School and Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

* Supporting Information

**ABSTRACT:** Conformational characteristics of poly(ethylene carbonate) (PEC) and poly(propylene carbonate) (PPC) have been revealed via molecular orbital (MO) calculations and nuclear magnetic resonance (NMR) experiments on model compounds with the same bond sequences as those of the polycarbonates. Bond conformations derived from the MO calculations on the models were in exact agreement with those from the NMR experiments. Both PEC and PPC were indicated to adopt distorted conformations including a number of gauche bonds and cover themselves with negative charges, thus failing to form a regular packing and remaining amorphous. The MO data were applied to the refined rotational isomeric state (RIS) calculations to yield conformational properties such as the characteristic ratio, its temperature coefficient, the configurational entropy, and average geometrical parameters of unperturbed PEC and PPC chains. In the RIS calculations on PPC, the regio- and stereosequences were generated according to the Bernoulli trial or Markov stochastic process. In consequence, it was shown that the configurational properties of PPC do not depend significantly on its regio- and stereoregularities. The internal energy contribution to rubberlike chain elasticity, calculated from the temperature coefficient of the characteristic ratio, has indicated the possibility that PEC and PPC will behave as elastomers. The practical applications and potential utilizations of the polycarbonates are discussed on the basis of the conformational characteristics and configurational properties.

**INTRODUCTION**

If noxious fumes generated in industrial processes were dispersed into the atmosphere, animals including human beings and plants would be seriously injured or, at their worst, killed. However, chemists have settled such problems by fixing the gases in solids. For example, in alkali industries, gaseous chlorine generated in sodium production has been chemically changed to useful polymers such as poly(vinyl chloride).\(^1\) As another example, one may mention carbon dioxide. Of course, carbon dioxide itself is not necessarily a harmful substance but, on the contrary, a nutrient source indispensable for plants. To suppress the global warming, however, we have been strongly required to control the amount of atmospheric carbon dioxide.

In 1969, Inoue, Koinuma, and Tsuruta\(^2,3\) reported a reaction scheme to synthesize poly(alkyl carbonate)s, that is, alternating copolymers of epoxides with carbon dioxide (Scheme 1). In the reaction, carbon dioxide itself is not necessarily a harmful substance but, on the contrary, a nutrient source indispensable for plants. To suppress the global warming, however, we have been strongly required to control the amount of atmospheric carbon dioxide.

In 1969, Inoue, Koinuma, and Tsuruta\(^4,5\) reported a reaction scheme to synthesize poly(alkyl carbonate)s, that is, alternating copolymers of epoxides with carbon dioxide (Scheme 1). In the reaction, carbon dioxide, the most inactive (i.e., thermodynamically dead) carbon source, is utilized. Because of the growing worldwide interest in global warming, polymer chemists and engineers have been paying particular attention to polycarbonates. If carbon dioxide emitted from combustion of natural gas, petroleum, and coal can be effectively absorbed on basic polymers such as poly(ethylene imine)\(^4−6\) and its derivatives\(^7\) and analogues,\(^8\) the polycarbonates may be produced from the collected gas, and consequently, CO\(_2\) fixation will be realized.

Of the aliphatic polycarbonates, PEC (Figure 1) and PPC were synthesized early\(^2,3\) but have not been easy to use either as hard plastics or as flexible rubbers because glass transitions of PEC and PPC occur around room temperature (ca. 20 °C) and human body temperature (35–40 °C), respectively.\(^9\) Therefore, the polycarbonates will become hard in cold areas (or seasons) but flexible in hot ones.

Inasmuch as PPC has an asymmetric carbon atom in the repeating unit, its primary structure is determined by two kinds...
of configurations: stereo- and regioisomerizations. The former means the existence of \((R)-\) and \((S)-\)isomers (see Figure 2). The latter means the formation of three kinds of linkages between the monomeric units: head-to-tail (abbreviated as \(H−T\)), head-to-head (\(H−H\)), and tail-to-tail (\(T−T\)) (see Figure 3). For these reasons, polymer chemists have challenged to develop stereospecific catalysts for controlling its regio- and stereoregularities\(^{10−22}\) in expectation that fully regular PPCs might crystallize and exhibit so large an elastic modulus and so high a glass transition temperature \((T_g)\) as to be used as hard plastics.

According to a cardinal principle of polymer science and molecular biology, “higher-order structures, physical properties, and functions of a polymer originate from its primary structure”\(^{26}\); it is of fundamental importance to reveal the conformational characteristics of PEC and PPC and, furthermore, to evaluate their configurational properties. This is the prime aim of this study. The conformational analysis of model compounds with the same bond sequences as those of the polycarbonates, ethylene glycol bis(methyl carbonate) \((E_{\text{model}})\) for PEC and propylene glycol bis(methyl carbonate) \((P_{\text{model}})\) for PPC, has been carried out by molecular orbital (MO) calculations and nuclear magnetic resonance (NMR) experiments. The MO energies and geometrical parameters were introduced into the refined RIS scheme\(^{23}\) to yield configurational properties of the two polycarbonates. Then, stochastic processes based on the Bernoulli trial and first-order Markov chain\(^{24,25}\) were employed to generate regio- and stereosequences of PPC to elucidate how its properties depend on the two kinds of configurations. Herein, the procedures and results are described in detail. On the basis of the structural information thus established, physical

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**Figure 1.** (a) PEC and (b) PPC. The bonds are designated as shown, and \(x\) is the degree of polymerization. To facilitate the refined rotational isomeric state (RIS) calculations, the polymeric chains have been assumed to be terminated by a methyl group.

**Figure 2.** Stereosequences of PPC: (a) \((R)-\) and (b) \((S)-\)isomers; (c) \((R,R)-\), (d) \((R,S)-\), (e) \((S,R)-\), and (f) \((S,S)-\)diads. \((R,R)-\) and \((S,S)-\)diad combinations are designated as \(\text{meso}\), and \((R,S)-\) and \((S,R)-\)diad ones as \(\text{racemo}\). When the polymeric chain is composed of only \(\text{meso}\) \((\text{racemo})\) couplings, the stereoregularity is termed isotactic (syndiotactic).

**Figure 3.** Regiosequences of PPC. Definition of (a) orthodromic \((O)\) and (b) antidromic \((A)\) directions. Four possible combinations of \((O)-\) and \((A)-\)directions between neighboring units: (c) \((O,O)\), head-to-tail \((H−T)\); (d) \((O,A)\), head-to-head \((H−H)\); (e) \((A,A)\), tail-to-head \((T−H)\); and (f) \((A,O)\), tail-to-tail \((T−T)\). The tail-to-head linkage is included in \(H−T\); therefore, the three expressions, \(H−T\), \(H−H\), and \(T−T\), are used herein.
properties, practical uses, and potential applications of PEC and PPC are discussed.

**RESULTS AND DISCUSSION**

**NMR Experiments.** Figure 5a shows ¹H NMR satellite peaks observed from the naturally abundant ¹³CH₂ group of the E_model. The spectrum simulation reproduced the observation well and yielded the J_HH and J_HH’ values. In Table 1, the two vicinal couplings are given for each NMR solvent and temperature. As explained in the “Methods” section, the p_t and p_g values were derived from eqs 8 and 9 with the two sets of J_T and J_G. The sum of p_t and p_g, thus obtained was slightly different from unity and hence divided by the sum to fulfill eq 10. The p_t values of bond 5 (Table 2) are so small as to indicate a strong gauche preference of the CH₂–CH₂ bond, and the p_t value tends to increase with temperature and decrease slightly with solvent polarity.

![Figure 4](image-url)  
Figure 4. Model compounds of PEC and PPC: (a) for PEC, ethane-1,2-diyl dimethyl bis(carbonate) (E_model) and (b) for PPC, dimethyl propane-1,2-diyl bis(carbonate) (P_model). As indicated, the bonds are designated, and the methylene and methine protons are labeled for NMR analysis. (R)- and (S)-P_models yield the identical NMR spectra; therefore, (R)-P_model is exclusively employed herein.

![Figure 5](image-url)  
Figure 5. Observed (above) and calculated (below) ¹H NMR spectra: (a) satellite from the CH₃ group of the E_model dissolved in dimethyl-d₆ sulfoxide (DMSO-d₆) at 25 °C; (b) H₆ (left), H₅ (middle), and H₄ (right) of the P_model dissolved in CDCl₃ at 25 °C. For the proton symbols of the P_model, see Figure 4.

**Table 1. Observed NMR Vicinal ¹H–¹H Coupling Constants of E_Model**

| solvent      | permittivity | temp (°C) | J_HH | J_HH’ |
|--------------|--------------|-----------|------|-------|
| chloroform-d | 4.8          | 15        | 6.46 | 2.70  |
|              |              | 25        | 6.46 | 2.81  |
|              |              | 35        | 6.46 | 2.89  |
|              |              | 45        | 6.45 | 2.97  |
|              |              | 55        | 6.44 | 3.05  |
| acetone-d₆   | 20.7         | 15        | 6.52 | 2.60  |
|              |              | 25        | 6.49 | 2.65  |
|              |              | 35        | 6.49 | 2.70  |
|              |              | 45        | 6.48 | 2.76  |
| methanol-d₆  | 32.7         | 15        | 6.48 | 2.58  |
|              |              | 25        | 6.47 | 2.61  |
|              |              | 35        | 6.46 | 2.67  |
|              |              | 45        | 6.46 | 2.75  |
|              |              | 55        | 6.46 | 2.82  |
| DMSO-d₆      | 46.7         | 25        | 6.49 | 2.48  |
|              |              | 35        | 6.49 | 2.53  |
|              |              | 45        | 6.48 | 2.60  |
|              |              | 55        | 6.47 | 2.69  |

*In Hz.

**Table 2. Trans Fractions (p_t’s) of E_Model: Comparison between MO Calculations and NMR Experiments**

| medium       | bond 4 (6) | bond 5 | NMR  |
|--------------|------------|--------|------|
|              | MO         | MO     |      |
|              | set A      | set B  |      |
| gas          | 15         | 0.39   | 0.12 |
|              | 25         | 0.39   | 0.12 |
|              | 35         | 0.39   | 0.13 |
|              | 45         | 0.39   | 0.13 |
|              | 55         | 0.38   | 0.14 |
| chloroform   | 15         | 0.51   | 0.06 |
|              | 25         | 0.50   | 0.07 |
|              | 35         | 0.50   | 0.07 |
|              | 45         | 0.49   | 0.07 |
|              | 55         | 0.49   | 0.08 |
| acetone      | 15         | 0.55   | 0.04 |
|              | 25         | 0.54   | 0.05 |
|              | 35         | 0.53   | 0.05 |
|              | 45         | 0.53   | 0.05 |
| methanol     | 15         | 0.55   | 0.04 |
|              | 25         | 0.55   | 0.04 |
|              | 35         | 0.54   | 0.05 |
|              | 45         | 0.53   | 0.05 |
|              | 55         | 0.53   | 0.06 |
| DMSO         | 25         | 0.55   | 0.04 |
|              | 35         | 0.54   | 0.05 |
|              | 45         | 0.53   | 0.05 |
|              | 55         | 0.53   | 0.06 |

In Figure 5b, ¹H NMR spectra observed from H₆, H₅, and H₄ of the P_model are shown, together with the spectrum simulations. The obtained J_AB and J_BC values (Table 3) were substituted into eqs 11 and 12 to yield the bond conformations as shown in Table 4. The magnitude relation of J_HH’ < J_HH < J_G always holds regardless of the solvent and temperature.

**MO Calculations.** Table 5 shows conformer free energies of the E_model. Of the eight conformers that the B3LYP optimization gave, the most stable conformation is tg+t (Figure 4).
Table 3. Observed NMR Vicinal $^1$H–$^1$H Coupling Constants of $P_{\text{Model}}$

| solvent     | temp (°C) | $J_{ac}$ | $J_{bc}$ |
|-------------|-----------|----------|----------|
| chloroform-d| 15        | 6.85     | 3.32     |
|             | 25        | 6.80     | 3.34     |
|             | 35        | 6.71     | 3.43     |
|             | 45        | 6.60     | 3.51     |
|             | 55        | 6.58     | 3.55     |
| acetone-d$_6$| 15        | 6.82     | 3.06     |
|             | 25        | 6.75     | 3.11     |
|             | 35        | 6.68     | 3.16     |
|             | 45        | 6.66     | 3.20     |
| methanol-d$_6$| 15        | 6.80     | 3.10     |
|             | 25        | 6.77     | 3.15     |
|             | 35        | 6.75     | 3.21     |
|             | 45        | 6.70     | 3.25     |
|             | 55        | 6.65     | 3.31     |
| DMSO-d$_6$  | 25        | 6.76     | 2.93     |
|             | 35        | 6.70     | 2.96     |
|             | 45        | 6.66     | 3.00     |
|             | 55        | 6.60     | 3.04     |

$n$Hz.

“Table 4. Bond Conformations of (R)-$P_{\text{Model}}$ Determined from NMR Experiments

| solvent | temp (°C) | bond  $g$ | set A | set B |
|---------|-----------|-----------|-------|-------|
|         |           | $P_l$     | $P_g$ | $P_p$ | $P_l$ | $P_g$ | $P_p$ |
| chloroform | 15       | 0.10      | 0.59  | 0.31  | 0.11  | 0.50  | 0.39  |
|          | 25       | 0.11      | 0.58  | 0.31  | 0.11  | 0.50  | 0.39  |
|          | 35       | 0.12      | 0.57  | 0.31  | 0.12  | 0.49  | 0.39  |
|          | 45       | 0.13      | 0.56  | 0.31  | 0.13  | 0.48  | 0.39  |
|          | 55       | 0.14      | 0.55  | 0.31  | 0.14  | 0.47  | 0.39  |
| acetone  | 15       | 0.07      | 0.56  | 0.37  | 0.08  | 0.50  | 0.42  |
|          | 25       | 0.08      | 0.55  | 0.37  | 0.09  | 0.49  | 0.42  |
|          | 35       | 0.08      | 0.54  | 0.38  | 0.10  | 0.48  | 0.42  |
|          | 45       | 0.09      | 0.53  | 0.38  | 0.10  | 0.48  | 0.42  |
| methanol | 15       | 0.08      | 0.55  | 0.37  | 0.09  | 0.49  | 0.42  |
|          | 25       | 0.08      | 0.55  | 0.37  | 0.09  | 0.49  | 0.42  |
|          | 35       | 0.09      | 0.55  | 0.36  | 0.10  | 0.49  | 0.41  |
|          | 45       | 0.10      | 0.54  | 0.36  | 0.11  | 0.48  | 0.41  |
|          | 55       | 0.10      | 0.54  | 0.36  | 0.11  | 0.48  | 0.41  |
| DMSO     | 25       | 0.05      | 0.55  | 0.40  | 0.07  | 0.49  | 0.44  |
|          | 35       | 0.06      | 0.54  | 0.40  | 0.07  | 0.49  | 0.44  |
|          | 45       | 0.06      | 0.54  | 0.40  | 0.08  | 0.49  | 0.44  |
|          | 55       | 0.07      | 0.53  | 0.40  | 0.08  | 0.47  | 0.45  |

6a), indicating a gauche preference of the central CH$_2$–CH$_2$ bond. It has been found that the aromatic and aliphatic esters with the C(==O)–O–CH$_2$–CH$_2$–O–C(==O) bond sequence show strong gauche preferences in the central CH$_2$–CH$_2$ bond. The free energies of the tgt conformation were evaluated as, for example, $-1.1$ kcal mol$^{-1}$ for poly(ethylene terephthalate) (PET) and $-1.2$ kcal mol$^{-1}$ for poly(ethylene succinate) (PES).$^{26,27}$ These $\Delta G_k$ values are comparable to that of PEC (Table 5). Therefore, it can be concluded that the tgt stability is inherent in the C(==O)–O–CH$_2$–CH$_2$–O–C(==O) sequence of the esters. The tgt conformer also has a small free energy of 0.1–0.3 kcal mol$^{-1}$ as compared with that of poly(ethylene oxide) (PEO) (1.3 kcal mol$^{-1}$).$^{28-30}$ It is also known that the tgt conformations of PET and PES have relatively small $\Delta G_k$ values of 0.5 and 0.3 kcal mol$^{-1}$, respectively.$^{26,27}$ In the tgt conformation (Figure 6b), a short C==O–C–H contact (2.40 Å) can be found between the carbonyl and methylene groups via the gauche O–CH$_2$ bond, and the involved O==C–O–CH$_2$–C–H atoms lie on a plane. The above results indicate that the PEC chain tends to adopt distorted structures with a number of gauche bonds. In Table 2, the bond conformations calculated from the $\Delta G_k$ values are listed. As for the CH$_2$–CH$_2$ bond, the MO calculations agree satisfactorily with set A and exactly with set B. These facts show the reliability of the MO energies.

Table 6 shows the $\Delta G_k$ values of $P_{\text{Model}}$. Its asymmetric carbon renders the $27 (=3^3)$ conformers unique and irreducible, and the pendant methyl group gives rise to intramolecular steric repulsions; however, $P_{\text{Model}}$ exhibits the conformational preferences and intramolecular interactions similar to those found for the $E_{\text{Model}}$. A number of conformers have negative $\Delta G_k$ values. In particular, those of g'g't and tg't and g'g'g are largely negative; therefore, PPC will also adopt distorted structures. The bond conformations of $P_{\text{Model}}$ calculated from the $\Delta G_k$ values, are listed in Table 7. For the CH$_2$–CH$_2$ bond, the magnitude relation $p_l < p_g < p_p$ holds, thus being consistent with the NMR analysis. On the basis of the good agreement between theory and experiment, we advanced to the refined RIS calculations on PEC and PPC with the $\Delta G_k$ energies and geometrical parameters (Tables S1 and S2, Supporting Information) of the models.

**Refined RIS Calculations.** The characteristic ratios ($\langle r^2 \rangle / n^2$), its temperature coefficients (dln$\langle r^2 \rangle / dT$), configurational entropies ($S_{\text{conf}}$), and averaged geometrical parameters of unperturbed PEC and PPC chains at 25 °C are presented in Table 8. The PPC chain was assumed to be isotactic and include only the H–T linkage. The temperature coefficient at $T_0$ was calculated by the finite-difference method

$$\frac{\ln\langle r^2 \rangle (T_0 + \Delta T)/\langle r^2 \rangle (T_0 - \Delta T)}{2\Delta T}$$

where $T_0$ and $\Delta T$ were set equal to 298.15 K (25 °C) and 1.00 K, respectively.

The $\langle r^2 \rangle / n^2$ values are 2.42–2.54 (PEC) and 2.26–2.36 (PPC), much smaller than those of PEO (5.2 at 34.5 °C),$^{20,32,33}$ PPO (6.0 at 50 °C),$^{31,34}$ and polyethylene (6.4–8.3 around 140 °C).$^{33-39}$ This is because both PEC and PPC have strong preferences for gauche conformations. The dln$\langle r^2 \rangle / dT$ values of PEC and PPC show solvent dependence; the values decrease with increasing solvent polarity. The temperature coefficient of PEC changes its sign between gas and chloroform, whereas that of PPC always stays positive. These results will be discussed in the “Mechanical Properties” section.

The configurational entropy (often termed conformational entropy) can be calculated from

$$S_{\text{conf}} = R \ln Z + T \frac{d(\ln Z)}{dT}$$

where $R$ is the gas constant, $x$ is the degree of polymerization, $T$ is the absolute temperature, and $Z$ is the partition function of the whole chain. At a phase transition such as melting, the $S_{\text{conf}}$ value corresponds to the entropy change at constant volume.
According to the (4.8) of chloroform; the RIS calculations are expected to f
regio- and stereosequences were also calculated. Then, the 
small S always satisfy

\[ S_{\text{conf}} = (\Delta S)_p - \Delta S_\beta \]

where \( \Delta S_\beta = (\alpha/\beta) \Delta V \) with \( \alpha \) and \( \beta \) being the thermal expansion coefficient and isothermal compressibility, respectively. The \( S_{\text{conf}}/(\Delta S)_p \) ratio has been estimated as, for example, 0.8–0.9 for polyethers and polythioethers and 0.5–0.7 for
polystyrenes, while amorphous elastomers exhibit comparatively small \( S_{\text{conf}}/(\Delta S)_p \) values such as 0.5 (natural rubber) and 0.6 (gutta percha). Therefore, amorphous PEC and PPC would also have somewhat smaller \( S_{\text{conf}}/(\Delta S)_p \) ratios than those of semicrystalline polymers.

The characteristic ratios of the PPC chains with different regio- and stereosequences were also calculated. Then, the \( \Delta G_k \) values on the chloroform solution were employed because the dielectric constant (ca. 3) of PPC is comparatively close to that (4.8) of chloroform; the RIS calculations are expected to represent the amorphous PPC chain. According to the Bernoulli trial, the \( \langle r^2 \rangle_{o/n}^2 \) value of the infinite PPC chain (degree of polymerization \( x = \infty \)) was calculated as a function of \( p_{\text{ortho}} \) and \( p_{\beta} \) as shown in Figure 7a. The \( p_{\text{ortho}} \) and \( p_{\beta} \) values change at an interval of 0.1. The stereo- and regioinversion \((R) \rightarrow (S) \) or \((S) \rightarrow (R) \) and regoinversion \((O) \rightarrow (A) \) or \((A) \rightarrow (O) \) were assumed to occur independently of each other (the independent-event model). In the Bernoulli trial, the calculated quantities \( f(p) \)’s always satisfy \( f(1 - p_{\text{ortho}}) = f(1 - p_{\text{ortho}}) \) and \( f(p_{\beta}) = f(1 - p_{\beta}) \) (see Table S3, Supporting Information); thus, the \( f(p) \) is symmetric with respect to \( p_{\text{ortho}} = 0.5 \) and \( p_{\beta} = 0.5 \). The average of \( f(p_{\text{ortho}}) \) and \( f(1 - p_{\text{ortho}}) \) is given in Table 8. Similarly, in the Markov process, such symmetries were considered, and the average values were adopted.

In Figure 7a, therefore, the \( \langle r^2 \rangle_{o/n}^2 \) value is plotted within ranges of 0.0 \( \leq p_{\text{ortho}} \leq 0.5 \) and 0.0 \( \leq p_{\beta} \leq 0.5 \). When \( p_{\beta} = 0.0 \) (isotactic), the characteristic ratio increases from 2.26 to 2.66 with increasing \( p_{\text{ortho}} \). In the range of \( p_{\beta} = 0.5 \) (atactic), the plotted data overlap each other at \( \langle r^2 \rangle_{o/n}^2 \approx 2.54 \); the stereochemically irregular PPC chains have almost the same average dimension independently of the regioregularity. It should be noted that the Bernoulli trial cannot generate the syndiotactic chain.

Most of the synthesized PPC chains keep the chirality of propylene oxide and include the H–T linkage predominantly. However, propylene oxide rarely undergoes abnormal ring-opening, and consequently, the PPC chain randomly includes adjoining H–H and T–T linkages, between which the chiral form is different from those of the neighbors; therefore, both stereo- and regioinversion \((R) \rightarrow (S) \) or \((S) \rightarrow (R) \) and regoinversion \((O) \rightarrow (A) \) or \((A) \rightarrow (O) \) occur simultaneously. However, the probability of the defect stays as small as several percent. Thus, the configuration of the PPC chain with the defects may be represented by the Bernoulli trial in which both regio- and stereoinversions are synchronized (the synchronous model). In Figure 7b, the characteristic ratios thus calculated are plotted as a function of \( p_{\beta} \) (see Table S3, Supporting Information). The plot is also symmetric with respect to \( p_{\beta} = 0.5 \). The curve can be seen to decrease gradually with an increase in \( p_{\beta} \); the synchronous inversions tend to render the PPC chain more contracted. However, the change in \( \langle r^2 \rangle_{o/n}^2 \) between \( p_{\beta} = 0.0 \) and \( p_{\beta} = 0.5 \) is ca. 10%.

In Figure 8a, the \( \langle r^2 \rangle_{o/n}^2 \) values calculated according to the Markov process are shown as a function of \( p_{\text{ortho}} = 0.5 \) and \( p_{\beta} \). Then, the \( p_{11-T} \) and \( p_{\text{meso}} \) values were changed from zero to unity at intervals of 0.1, and the contour lines in Figure 8 were drawn by interpolating the two-dimensional data meshes. In \( p_{\text{meso}} = 0.0 \) (syndiotactic), the \( \langle r^2 \rangle_{o/n}^2 \) value increases from 1.98 to 2.80 with increasing \( p_{11-T} \) whereas, in \( p_{\text{meso}} = 1.0 \) (isotactic), it decreases from 3.08 to 2.26. Therefore, its maximum can be found at \( p_{\text{meso}} = 1.0 \) and \( p_{11-T} = 0.0 \): either \((O,R)\)- and \((A,R)\)-units of \((O,S)\)- and \((A,S)\)-units are arranged alternately. The minimum \( \langle r^2 \rangle_{o/n}^2 \) (≈2.0) is essentially equal to that (≈2.0) of the above synchronous model of \( p_{\beta} = p_{\text{ortho}} = 0.5 \) and located at the origin, \( p_{\text{meso}} = p_{11-T} = 0.0 \), where either \((O,R)\)- and \((A,S)\)-

*Table 5. Conformer Free Energies (\( \Delta G_k \)'s) of Model Compounds of PEC and PEO, Evaluated by Ab Initio MO Calculations*.

| k | conformation | gas | chloroform | acetone | methanol | DMSO | PEO | gas |
|---|--------------|-----|------------|---------|----------|------|------|-----|
| 1 | t t t        | 0.00| 0.00       | 0.00    | 0.00     | 0.00 | 0.00 |     |
| 2 | t t g'       | 0.11| 0.23       | 0.28    | 0.29     | 0.29 | 1.31 |     |
| 3 | t g' t       | -0.81| -1.35     | -1.59   | -1.62    | -1.64| 0.19 (−0.08') |     |
| 4 | t g' g'      | -0.59| -1.00     | -1.20   | -1.23    | -1.25| 1.28 |     |
| 5 | t g' g'      | (absent) |     |     |     |     |     |     |
| 6 | g' t t       | 1.90| 1.89       | 1.85    | 1.84     | 1.84 | 2.74 |     |
| 7 | g' t g'      | 0.59| 0.82       | 0.87    | 0.88     | 0.88 | 2.61 |     |
| 8 | g' g' g'     | -0.42| -0.45     | -0.48   | -0.49    | -0.49| 2.27 |     |
| 9 | g' g' g'     | -0.72| -0.81     | -0.89   | -0.90    | -0.91| 1.88 |     |
| 10| g' g' g'     | (absent) |     |     |     |     |     |     |

The average of \( f(p_{\text{ortho}}) \) and \( f(1 - p_{\text{ortho}}) \) is given in Table 8. Similarly, in the Markov process, such symmetries were considered, and the average values were adopted.

In Figure 6, \( E \) model, (a) tg't, electrostatic potential distribution and (b) tgg', an intramolecular C=O–H–C close contact (dotted line) with the O–H distance of 2.40 Å.

Figure 6. E model: (a) tg’t, electrostatic potential distribution and (b) tgg’, an intramolecular C=O–H–C close contact (dotted line) with the O–H distance of 2.40 Å.

The average of \( f(p_{\text{ortho}}) \) and \( f(1 - p_{\text{ortho}}) \) is given in Table 8. Similarly, in the Markov process, such symmetries were considered, and the average values were adopted.
Table 6. Conformer Free Energies ($\Delta G_i$s) of PPC and Poly(propylene oxide) (PPO), Evaluated by Ab Initio MO Calculations$^a$ 

| $k$ | conformation$^d$ | gas | chloroform | acetone | methanol | DMSO | \( \Delta G_i \) | gas | PPO |
|-----|-----------------|-----|------------|---------|----------|------|----------------|-----|------|
| 1   | t t t           | 0.00| 0.00       | 0.00    | 0.00     | 0.00 | 0.00           | 0.00| 0.00 |
| 2   | t t g$^*$       | 2.22| 2.36       | 2.41    | 2.42     | 2.42 | 3.20           |      |      |
| 3   | t t g$^-$       | -0.15| -0.18     | -0.18   | -0.18    | -0.18 | 0.43          |      |      |
| 4   | t g$^*$ t       | -0.47| -1.07     | -1.31   | -1.34    | -1.36 | 0.62          |      |      |
| 5   | t g$^*$ g$^*$   | 2.28| 1.82       | 1.58    | 1.55     | 1.53 | 3.80          |      |      |
| 6   | t g$^*$ g$^-$   | (absent)$^e$ |         |         |         |      | -0.20         |      |      |
| 7   | t g$^*$ t       | -0.06| -0.58     | -0.64   | -0.68    | -0.90 | 1.57          |      |      |
| 8   | t g$^*$ t       | 5.06| 4.32       | 3.91    | 3.85     | 3.82 | 2.18          |      |      |
| 9   | t g$^*$ g$^-$   | -0.22| -0.70     | -0.95   | -0.98    | -1.00 | 1.38          |      |      |
| 10  | g$^*$ t t       | (absent)$^e$ |         |         |         |      | (absent)$^e$ |      |      |
| 11  | g$^*$ t g$^*$   | (absent)$^e$ |         |         |         |      | (absent)$^g$ |      |      |
| 12  | g$^*$ t g$^-$   | (absent)$^e$ |         |         |         |      | (absent)$^g$ |      |      |
| 13  | g$^*$ g$^*$ t   | -0.78| -1.22     | -1.39   | -1.42    | -1.43 | 2.30          |      |      |
| 14  | g$^*$ g$^*$ g$^*$ | 2.02| 2.02       | 2.02    | 2.00     | 2.00 | 4.02          |      |      |
| 15  | g$^*$ g$^*$ g$^-$ | 2.19| 1.13       | 0.69    | 0.62     | 0.59 | 1.34          |      |      |
| 16  | g$^*$ g$^*$ t   | (absent)$^e$ |         |         |         |      | 0.99          |      |      |
| 17  | g$^*$ g$^*$ g$^*$ | (absent)$^e$ |         |         |         |      | (absent)$^e$ |      |      |
| 18  | g$^*$ g$^*$ g$^-$ | -0.59| -0.78     | -0.90   | -0.92    | -0.93 | 1.51          |      |      |
| 19  | g$^*$ t t       | 0.12| 0.18       | 0.20    | 0.20     | 0.20 | 1.25          |      |      |
| 20  | g$^*$ g$^*$ t   | 2.64| 2.86       | 2.91    | 2.92     | 2.92 | 4.46          |      |      |
| 21  | g$^*$ t g$^-$   | (absent)$^e$ |         |         |         |      | 1.87          |      |      |
| 22  | g$^*$ g$^*$ t   | (absent)$^e$ |         |         |         |      | 0.80          |      |      |
| 23  | g$^*$ g$^*$ g$^*$ | 2.28| 2.12       | 1.98    | 1.96     | 1.95 | 4.28          |      |      |
| 24  | g$^*$ g$^*$ g$^-$ | (absent)$^e$ |         |         |         |      | (absent)$^e$ |      |      |
| 25  | g$^*$ g$^*$ t   | 0.33| -0.11      | -0.34   | -0.37    | -0.39 | (absent)$^e$ |      |      |
| 26  | g$^*$ g$^*$ g$^*$ | 5.14| 4.73       | 4.48    | 4.44     | 4.42 | (absent)$^e$ |      |      |
| 27  | g$^*$ g$^*$ g$^-$ | 0.13| -0.13      | -0.27   | -0.29    | -0.30 | (absent)$^e$ |      |      |

$^a$In kcal mol$^{-1}$, relative to the all-trans conformation. $^b$From (R)-P$_{model}$, at the MP2/6-311+G(2d,p)//B3LYP/6-311+G(2d,p) level. $^c$From (R)-1,2-dimethoxypropane, at the MP2/6-31+G(d)//HF/6-31G(d) level.$^{31}$ $^d$In the O−CH$_2$−CH(CH$_3$)−O bond sequence. $^e$Local minimum of the potential was not found by the geometrical optimization.

Table 7. Bond Conformation of (R)-P$_{Model}$, Evaluated from MO Calculations

| medium | temp ($^\circ$C) | bond 4 | bond 5 | bond 6 |
|--------|-----------------|--------|--------|--------|
| gas    | 15              | 0.44   | 0.42   | 0.14   |
|        | 25              | 0.45   | 0.41   | 0.14   |
|        | 35              | 0.45   | 0.40   | 0.15   |
|        | 45              | 0.45   | 0.40   | 0.15   |
|        | 55              | 0.46   | 0.39   | 0.15   |
| chloroform | 15 | 0.49   | 0.41   | 0.10   |
|        | 25              | 0.49   | 0.40   | 0.11   |
|        | 35              | 0.49   | 0.40   | 0.11   |
|        | 45              | 0.49   | 0.39   | 0.12   |
|        | 55              | 0.49   | 0.39   | 0.12   |
| acetone | 15             | 0.51   | 0.39   | 0.10   |
|        | 25              | 0.51   | 0.39   | 0.10   |
|        | 35              | 0.51   | 0.38   | 0.11   |
|        | 45              | 0.51   | 0.38   | 0.11   |
| methanol | 15          | 0.51   | 0.39   | 0.10   |
|        | 25              | 0.52   | 0.38   | 0.10   |
|        | 35              | 0.52   | 0.38   | 0.10   |
|        | 45              | 0.52   | 0.37   | 0.11   |
|        | 55              | 0.52   | 0.37   | 0.11   |
| DMSO   | 15              | 0.52   | 0.37   | 0.10   |
|        | 25              | 0.52   | 0.38   | 0.10   |
|        | 35              | 0.52   | 0.38   | 0.10   |
|        | 45              | 0.52   | 0.37   | 0.11   |
|        | 55              | 0.52   | 0.37   | 0.11   |
units or (A,R)- and (O,S)-units are arranged alternately (the synchronous inversions).

Characteristics of the Polycarbonate Chains. It is known that PEO crystallizes in the tgt conformation. As our MO calculations indicate, PEC is also most stabilized in this conformation. Nevertheless, PEC is an amorphous polymer. MO calculations indicate, PEC is also most stabilized in this gauche bonds. This is also an origin.

Strongly prefer distorted conformations including a number of characteristic ratios (⟨r²⟩/n²) of PPC, derived from the refined RIS calculations with the MO parameters including solvent effects. Inasmuch as amorphous PEC and PPC chains lie in near unperturbed states, the refined RIS calculations can provide reliable insights into their solid-state properties as well as solution (melt) properties. Because of the distorted conformations, PEC and PPC exhibit the characteristic ratios smaller than those of common linear polymers. The RIS calculations with the Markov chain showed that the characteristic ratio of PPC does not depend significantly on the regio- and stereoregularities. The reason may be explained as follows. The carbonate group separates the neighboring rotatable O C and stereosequences were generated independently of each other, and the ⟨r²⟩/n² values are plotted against P_R for different P_ortho and (P_{1−T−} P_{1−T}) values: 0.0 and (1.00, 0.00, 0.00) (open circle); 0.10 and (0.82, 0.09, 0.09) (filled circle); 0.20 and (0.68, 0.16, 0.16) (open square); 0.30 and (0.58, 0.21, 0.21) (filled square); 0.40 and (0.52, 0.24, 0.24) (open triangle); and 0.50 and (0.50, 0.25, 0.25) (filled triangle). (b) Synchronous model the regio- and stereoregularities have no significant effects on the spatial conformation and probably on the other physical properties.

Mechanical Properties. Flory et al. thermodynamically revealed the requirement for rubberlike elasticity of polymers. On this basis, we can discuss whether amorphous PEC and PPC will exhibit rubberlike chain elasticity.

Figure 7. Characteristic ratios (⟨r²⟩/n²) of PPC derived from the refined RIS calculations with the Bernoulli trial. (a) (Independent-event model) the regio- and stereosequences were generated independently of each other, and the ⟨r²⟩/n² values are plotted against P_R for different P_ortho and (P_{1−T−} P_{1−T}) values: 0.0 and (1.00, 0.00, 0.00) (open circle); 0.10 and (0.82, 0.09, 0.09) (filled circle); 0.20 and (0.68, 0.16, 0.16) (open square); 0.30 and (0.58, 0.21, 0.21) (filled square); 0.40 and (0.52, 0.24, 0.24) (open triangle); and 0.50 and (0.50, 0.25, 0.25) (filled triangle). (b) Synchronous model the regio- and stereoregularities are changed synchronously: (O,R) → (A,S), (A,R) → (O,S), (O,S) → (A,R), or (A,S) → (O,R). The solid line represents a cubic function fitted to the calculated data (open circle).

Table 8. Geometrical Parameters of PEC and Isotactic (R)-PPC at 25 °C, Evaluated from the Refined RIS Calculations with MO Parameters Including Solvent Effects

| Gas          | Chloroform | Acetone | Methanol | DMSO |
|--------------|------------|---------|----------|------|
| ⟨r²⟩/n²      | 2.42       | 2.52    | 2.54     | 2.54 |
| (K⁻¹)       | 0.32       | −0.12   | −0.25    | −0.26 |
| S_cal (cal K⁻¹ mol⁻¹) | 5.51       | 5.16    | 4.97     | 4.94 |
| f/fo/×10³    | 95         | −35     | −73      | −78  |
| Geometry     |            |         |          |      |
| (chloroform) |            |         |          |      |
| Bond        | Bond       | Bond    | Bond     | Bond |
| a           | 1.339      | 107.9   | 0.0      |      |
| b           | 1.339      | 115.5   | 0.0      |      |
| c           | 1.440      | 110.0   | 0.0      | 95.5 |
| d           | 1.510      | 110.0   | 0.0      | 111.9|
| e           | 1.440      | 115.5   | 0.0      | 95.5 |
| ⟨r²⟩/n²      | 2.36       | 2.26    | 2.26     | 2.26 |
| (K⁻¹)       | 1.07       | 0.44    | 0.24     | 0.20 |
| S_cal (cal K⁻¹ mol⁻¹) | 4.34       | 4.12    | 4.05     | 4.04 |
| f/fo/×10³    | 320        | 130     | 72       | 60   |

Geometrical parameters averaged at 25 °C with the MO energies on the chloroform solution. Symbols: ⟨r⟩, averaged bond length (in Å); ⟨θ⟩, averaged bond angle (in deg); ⟨Φ⟩, average dihedral angle (in deg) of the ξ conformation.
The tension \( f \) of an elastomer is composed of two terms due to internal-energy \( (U) \) and entropy \( (S) \) changes\(^\text{46}\):

\[
f = f_U + f_S
\]

where

\[
f_U = \left( \frac{\partial U}{\partial L} \right)_{T,V}
\]

and

\[
f_S = -T \left( \frac{\partial S}{\partial L} \right)_{T,V}
\]

with \( T, V, \) and \( L \) being the absolute temperature, volume, and length, respectively. The \( f_U/f \) ratio is expressed as a function of the temperature coefficient of the mean square end-to-end distance by\(^\text{47-50}\):

\[
\frac{f_U}{f} = -T \left[ \frac{\partial \ln(f/T)}{\partial T} \right]_{L,V} = T \frac{d \ln(r^2_h)}{dT}
\]

Although intermolecular interactions occur in rubberlike materials, these interactions have been assumed to be independent of the configurations of the network chains. In other words, it is well-established that rubberlike elasticity is principally of intramolecular origin\(^\text{48,50,52}\). Therefore, we are allowed to discuss the possibility that the two polycarbonates will act as elastomers, on the basis of eq 7, which can be evaluated from the refined RIS calculations.

The \( f_U/f \) ratios of PEC and isotactic PPC of 100% H–T linkage at 25 °C were evaluated from the \( \ln(r^2)_0/dT \) values (in Table 8). The PEC chain has a positive value of 0.095 in the gas phase but negatives of −0.035 to −0.080 in the solvents, whereas PPC always shows positive values (0.32–0.52). For both polycarbonates, the \( f_U/f \) ratio tends to decrease with increasing medium polarity. The sign of \( f_U/f \) can be related to conformational changes during chain deformation as follows.

It is known that polyethylene shows negative \( f_U/f \) values of ca. −0.4\(^\text{47,49,50}\). Its \( \text{CH}_2–\text{CH}_2 \) bond prefers the trans conformation, and the trans-gauche energy difference is 0.4–0.5 kcal mol\(^{-1}\)\(^\text{35,53}\). As temperature increases \( (AT > 0) \), the trans conformations partly change to distorted gauche states of higher energy, and hence the chain dimension decreases \( (\Delta L) < 0 \), and \( \Delta U > 0 \), accordingly, \( d\ln(r^2)_0/dT < 0 \), \( \Delta U/\Delta L \approx (\partial U/\partial L) < 0 \), and \( f_U/f < 0 \). The negative \( f_U/f \) works against the entropic elasticity because the \( f_S \) term must always be positive.

The PPC chain gives positive \( f_U/f \) values. This is because, in contrast to polyethylene, PPC by nature causes distorted conformations such as \( \text{g}' \text{g} + \text{t} \), \( \text{g}' \text{g} \text{g} ' \text{g} + \text{t} \), \( \text{g}' \text{t} \text{g} ' \text{t} \), and \( \text{g}' \text{t} \text{g} ' \text{t} \). As the temperature is increased, the distortion is released by the gauche-to-trans change, and hence, the chain is extended: \( d\ln(r^2)_0/dT > 0 \). The stretching (contraction) of the PPC chain increases (decreases) the internal energy: \( (\partial U/\partial L) > 0 \), therefore, \( f_U/f > 0 \). The conformational characteristic of PPC supports its entropic elasticity. On the other hand, PEC changes the sign of \( f_U/f \), depending on the surroundings. It is well-known that elastomers give positive \( f_U/f \) values: cis-1,4-polybutadiene (0.10–0.17), polydimethylsiloxane (0.13–0.30), and natural rubber (0.12–0.18).\(^\text{50}\) Therefore, the PPC chain may be more likely than PEC to behave as an elastomer.

The \( f_U/f \) ratios of PPC were calculated according to the Markov model as a function of \( p_{H–T} \) and \( p_{\text{neat}} \). In Figure 8b, the data are also plotted as a two-dimensional contour map. The maximum \( f_U/f \) value (0.311) is found at the origin \( (p_{H–T} = p_{\text{neat}} = 0) \), where the minimum characteristic ratio was predicted above, and the PPC chain is a perfect alternating copolymer of either (\( O,R \))- and (\( A,S \))-monomers or (\( O,S \))- and (\( A,R \))-monomers. The minimum \( f_U/f \) (0.075) is indicated to be located at the left top corner \( (p_{H–T} = 0 \) and \( p_{\text{neat}} = 1) \), where the maximum \( r^2_0/n^2 \) was suggested, and the PPC chain is an alternating copolymer of either (\( O,R \))- and (\( A,R \))-units or (\( O,S \))- and (\( A,S \))-units. These facts suggest an inverse correlation between \( f_U/f \) and \( r^2_0/n^2 \), that is, between the rubberlike elasticity and the chain dimension.

It has been reported that PPC with a low \( T_g \) of ca. 10 °C behaves as an elastomer at room temperature with an elongation at break greater than 600% and completely recovers to the initial length after removal of the load.\(^\text{54}\) On the other hand, mechanical properties of PPC are more complicated owing to its higher g of 35–42 °C. Although PPC is brittle below 20 °C, an effective plasticizer (10 wt % of 1,6-bis[methyl urethane]hexane) was found to reduce \( T_g \) of PPC significantly and improve the mechanical properties: elongation at break, ca. 700% and tensile strength, 30 MPa.\(^\text{55}\) In addition, PPC was mixed with rubber polyurethane particles (30 wt %) to show an impact strength of as much as 228.3 J m\(^{-1}\).\(^\text{56}\) When amorphous PPC was blended and fixed by graft polymerization
with poly(β-hydroxybutyrate-co-hydroxyvalerate) (PHBV) (PHBV/PPC = 30:70 in weight), the composite materials exhibited a marked elongation at break of 1300%. In addition, block copolymers of PPC with poly(ethylene glycol), having weight-average molecular weights of 81 000 and 225 000, were shown to be stretchable up to 870 and 720%, respectively, even though the PPC alone was so brittle as to be broken at only a 7% extension. Accordingly, effective processing such as copolymerization, cross-linking, blending, and plasticizing for PEC and PPC will reveal their potential mechanical properties.

On Applications of PEC and PPC. Another expectable utilization of PEC and PPC is ion-conductive polymer electrolytes. As a representative polymer for this purpose, we can mention PEO. It is known that PEO is capable of changing the conformational preference according to the environment. In the gas phase or nonpolar media, the energy difference between tgt and tgt states in the O−CH2−CH2−O bond is close to null. In polar solvents, however, the tgt conformation and captures a cation such as alkali metal ions. Inasmuch as PEO is semicrystalline, the cations will be trapped readily capture, for example, Li+ ion. In addition, PEC and PPC are completely amorphous, and hence most monomeric units are ready to accept Li+ ions. Compared with PEO, therefore, the O

conductivity of PEO is reported to be on the order of 5.2 × 10−4 Sc m−1.61 As can be seen from Table 6, stable conformations in the O−CH2−C∗H−(CH2)−O bond sequence of P_model are tgt, tgt, tgt, tgt, g∗g, g∗g, and g∗g g∗, and hence amorphous PPC can also capture Li+ ion effectively. For a PCP/(H4Sb)2P(DCA)2Cl2 composite, the following electric characteristics have been reported: ionic conductivity, 5.2 × 10−4 S cm−1; electrochemical window, 4.6 V; and ionic transference number, 0.75.63 The green polymers synthesized similarly except that propylene glycol bis(methyl carbonate) (P_model) was used instead of ethylene glycol. The yield was 50%.

NMR Measurements. Proton NMR spectra were recorded at 500 MHz on a JEOL JNM-ECA500 spectrometer in the Center for Analytical Instrumentation of Chiba University. The sample temperature was increased stepwise from 15 or 25 °C to 45 or 55 °C at intervals of 10 °C. Free induction decays (FIDs) were accumulated under the following conditions: scan, 32−128; 45° pulse width, 5.7 μs; acquisition time, 4.4 s; and recycle delay, 4 s. The FID was fully zero-filled prior to the Fourier transform to yield enough digital resolution in Hz for the subsequent analysis. The NMR solvents were chloroform-d3 acetone-d6 methanol-d4 and dimethyl-3 sulfoxide (DMSO-d6), and 5 mm NMR sample tubes were used. The obtained spectra were simulated with the gNMR program to yield 1H chemical shifts and 1H−1H coupling constants.

NMR Analysis. Vicinal 1H−1H coupling constants (JHH and JHHHS) observed from the methylene protons, A, A’, B, and B’ of E_model (see Figures 4 and 9) can be expressed as weight averages of J1’s and JG’s

\[ J_{HH} = J_{AB} = J_{AF} = J_{P_1} + \frac{J_{T} + J_{G}}{2} p_G^1 \]

and

\[ J_{HH} = J_{AB} = J_{AF} = J_{T} + \frac{J_{G}}{2} p_G^1 \]

where the weights, p₁, and p₁ are trans and gauche fractions of the CH2−CH2 bond, respectively. By definition, we have

\[ p_1 + p_0 = 1 \]

where \( p_0 = p_0^* = p_0/2 \).

There is the possibility that P_model is either (R)- or (S)-isomer, but both give the identical NMR spectra. Therefore, although we employed its racemic mixture in NMR measurements, we are allowed to analyze the observed spectra with either isomeric model. Herein, the (R)-P_model is used throughout. Vicinal coupling constants between the methylene (A or B) and methine (C) protons are expressed as

\[ J_{AC} = J_{AC} + J_{AP_1} + J_{CP_0}^* + J_{CP_0}^* \]

and

\[ J_{BC} = J_{BC} + J_{BP_1} + J_{CP_0}^* + J_{CP_0}^* \]

For J1’s and JG’s, see Figure 9. The trans, gauche, and gauche− fractions fulfill

CONCLUSIONS

Conformational characteristics and configurational properties of PEC and PPC have been elucidated by the methodology based on MO calculations, NMR experiments, and RIS calculations. Both PEC and PPC were found to strongly prefer distorted conformations including a number of gauche states. In the RIS calculations on PPC, the Bernoulli and Markov stochastic processes were employed to generate its regio- and stereosequences, and its configurational properties were shown not to depend significantly on the regio- and stereosequences. The physical properties, practical uses, and potential applications of the two polycarbonates have been discussed in terms of the structural information thus obtained. In conclusion, as a result of the detailed computational characterization, it is preferable that PEC and PPC should be prepared at low costs so as to give high yields without paying particular attention to the regio- and stereoregularities, processed so as to lower the glass transition temperatures, and used as high-value added flexible functional materials.

METHODS

Synthesis of Model Compounds. Methyl chloroformate (9.7 mL, 0.125 mol), dissolved in chloroform (12.5 mL), was added dropwise under argon atmosphere to ethylene glycol (2.8 mL, 0.05 mol) and pyridine (20 mL), and the mixture was stirred at 0 °C for 3 h and then at room temperature overnight. The reaction mixture was acidified to pH = 2 with hydrochloric acid (20 mL) and underwent extraction twice with chloroform (15 mL × 2). The organic layer was washed thrice with saturated solution of sodium bicarbonate (30 mL × 3) and dried over anhydrous sodium sulfate (ca. 10 g) overnight. The solution was filtrated and condensed on a rotary evaporator. The residue was dried in vacuo at 35 °C for 3 h to yield ethylene glycol bis(methyl carbonate) (E_model) (yield, 86%).

Propylene glycol bis(methyl carbonate) (P_model) was synthesized similarly except that propylene glycol was used instead of ethylene glycol. The yield was 50%.

NMR Measurements. Proton NMR spectra were recorded at 500 MHz on a JEOL JNM-ECA500 spectrometer in the Center for Analytical Instrumentation of Chiba University. The sample temperature was increased stepwise from 15 or 25 °C to 45 or 55 °C at intervals of 10 °C. Free induction decays (FIDs) were accumulated under the following conditions: scan, 32−128; 45° pulse width, 5.7 μs; acquisition time, 4.4 s; and recycle delay, 4 s. The FID was fully zero-filled prior to the Fourier transform to yield enough digital resolution in Hz for the subsequent analysis. The NMR solvents were chloroform-d3 acetone-d6 methanol-d4 and dimethyl-3 sulfoxide (DMSO-d6), and 5 mm NMR sample tubes were used. The obtained spectra were simulated with the gNMR program to yield 1H chemical shifts and 1H−1H coupling constants.

NMR Analysis. Vicinal 1H−1H coupling constants (JHH and JHHHS) observed from the methylene protons, A, A’, B, and B’ of E_model (see Figures 4 and 9) can be expressed as weight averages of J1’s and JG’s

\[ J_{HH} = J_{AB} = J_{AF} = J_{P_1} + \frac{J_{T} + J_{G}}{2} p_G^1 \]

and

\[ J_{HH} = J_{AB} = J_{AF} = J_{T} + \frac{J_{G}}{2} p_G^1 \]

where the weights, p₁, and p₁ are trans and gauche fractions of the CH2−CH2 bond, respectively. By definition, we have

\[ p_1 + p_0 = 1 \]

where \( p_0 = p_0^* = p_0/2 \).

There is the possibility that P_model is either (R)- or (S)-isomer, but both give the identical NMR spectra. Therefore, although we employed its racemic mixture in NMR measurements, we are allowed to analyze the observed spectra with either isomeric model. Herein, the (R)-P_model is used throughout. Vicinal coupling constants between the methylene (A or B) and methine (C) protons are expressed as

\[ J_{AC} = J_{AC} + J_{AP_1} + J_{CP_0}^* + J_{CP_0}^* \]

and

\[ J_{BC} = J_{BC} + J_{BP_1} + J_{CP_0}^* + J_{CP_0}^* \]

For J1’s and JG’s, see Figure 9. The trans, gauche, and gauche− fractions fulfill
Gibbs free energy, being expressed as the difference of conformer free energy was obtained from the MP2 electronic energy calculations at the MP2/6-311+G(2d,p) level for the optimized geometry. The electronic energy was further calculated at the polarizable continuum model using the integral equation formalism. Substitution of the observed $J$ values into the above equations yields $p_t$ and $p_g$ of E_model or $p_{T,R}$ and $p_{T,R}^*$ of P_model, if the $J_t$ and $J_g$ values are given beforehand. This study has adopted two sets of $J_t$ and $J_g$ couplings used in in eqs 8, 9, 11, and 12 are defined as illustrated.

$$p_t + p_g + p_{g^*} = 1$$  \hspace{1cm} (13)

It should be noted that the gauche$^+$ and gauche$^-$ states are not equivalent: $p_t \neq p_g$. Substitution of the observed $J$ values into the above equations yields $p_t$ and $p_g$ of E_model or $p_{T,R}$ and $p_{T,R}^*$ of P_model, if the $J_t$ and $J_g$ values are given beforehand. This study has adopted two sets of $J_t$ and $J_g$: set A, $J_t's = 9.87$ and $J_g's = 2.54$ Hz for the chloroform solution and $J_t's = 10.25$ and $J_g's = 2.52$ Hz for the acetone, methanol, and DMSO solutions (taken from those of cis-2,6-dimethyl-1,4-dioxane); set B, $J_t's = 9.87$ and $J_g's = 2.54$ Hz for the chloroform solution and $J_t's = 10.25$ and $J_g's = 2.52$ Hz for the acetone, methanol, and DMSO solutions (taken from those of cis-2,6-dimethyl-1,4-dioxane).

**Figure 9.** Rotamers around bonds (a) 4 of E_model and P_model, (b) 5 of E_model, (c) 5 of (R)-P_model, and (d) 6 of E_model (R = H) and (R)-P_model (R = CH$_3$) models. For the bond numbers, see Figure 4. The vicinal $J_t$ and $J_g$ couplings used in eqs 8, 9, 11, and 12 are defined as illustrated.

**Molecular Orbital Calculations.** MO calculations on the model compounds were carried out with the Gaussian 09 program installed on an HPC Systems 5000-Z800 computer. For each conformer, the molecular geometry was fully optimized at the B3LYP/6-311+G(2d,p) level under the tight convergence, and thermochemical energies at 25 °C and 1 atm were also computed by the frequency calculation at the same level. Furthermore, the electronic energy was calculated at the MP2/6-311+G(2d,p) level for the optimized geometry. The conformer free energy was obtained from the MP2 electronic energy and the B3LYP thermochemical correction term to the Gibbs free energy, being expressed as the difference ($\Delta G_{\text{Gibbs}}$, $k$ conformer) from that of the all-trans conformation. The solvent effect on the MP2 electronic energy was evaluated by the polarizable continuum model using the integral equation formalism.

**Rotational Isomeric State Calculation.** The refined RIS scheme was applied to PEC and PPC. The refined RIS scheme has been developed so as to change both conformational energy and geometrical parameters with conformations of the neighboring as well as current bonds to yield accurate results. The statistical weight matrices of PEC and PPC were formulated on the basis of the chemical structures shown in Figure 1 and as presented in Appendices A and B (Supporting Information). The geometrical parameters of PEC and PPC were chosen from the optimized structures of E_model and P_model, respectively, being tabulated in Tables S1 and S2 (Supporting Information).

Conventionally, the C*H(CH$_3$)$_2$ and CH$_3$ parts of PPC have been termed head and tail, respectively. Herein, the CH$_2$ → C*H(CH$_3$)$_2$ (tail → head) and C*H(CH$_3$)$_2$ → CH$_3$ (head → tail) directions are designated as orthodromic (O) and antidromic (A), respectively (see Figure 3). However, this definition is not absolute: if the (O)-isomer is turned around 180° with respect to a line perpendicular to the chain axis, it becomes the (A)-isomer. Nevertheless, the RIS scheme requires us to determine the moving direction for the matrix multiplication. For example, when the monomer (propylene oxide + carbonate) has the O direction and (R)-chiral center, it is represented herein as (O,R)-monomer. The OO, OA, AA, and AO combinations between monomers form H−T, H−H, T−H, and T−T linkages, respectively, as illustrated in Figure 3. Inasmuch as the H−T and T−H linkages are identical, the regiosequences expressed in the O and A manner can be rewritten in terms of H−T, H−H, and T−T.

If we obtain conformer free energies of (O,R)-monomer of PPC and formulate its statistical weight matrices $U_i's$ (j: bond number), we can derive $U_i's$ of (O,S), (A,R), and (A,S)-monomers by proper matrix operations as shown in Appendix B (Supporting Information). From the optimized geometrical parameters of (O,R)-monomer (Table S2, Supporting Information), we can also derive those of the other three isomers.

To arrange the stereo- and regiosequences of the PPC chain, we have adopted two stochastic processes: the Bernoulli trial and the first-order Markov chain. In the Bernoulli trial, a random number was generated between zero and unity. When the number was smaller than or equal to the given $p_B$ value, the next repeating unit was (R)-isomer. Otherwise, (S)-isomer was selected. Here, $p_B$ represents the (R)-isomeric probability. The regiosequences were determined similarly with the $O$ probability ($p_{\text{ortho}}$) instead of $p_B$. The operation was repeated up to a given degree ($x$) of polymerization over a given number ($n$) of chains. Fractions of the regio- (H−T, H−H, and T−T) and stereosequences (diad, meso, and racemo; triad, mm, mr, rm, and rr) were calculated as a function of $p_b$ and $p_{\text{ortho}}$ according to the Bernoulli trial as given in Table S3 (Supporting Information).

In the Markov process, a random number was generated within the range of zero to unity. When the value was smaller or equal to $p_{\text{meso}}$ (or $p_{\text{H→T}}$), the same optical isomer (direction) as that of the preceding monomer was added. Otherwise, the other isomer (orientation) was added. Here, $p_{\text{meso}}$ and $p_{\text{H→T}}$ are probabilities of meso diad and H−T linkage, respectively. This operation was repeated $x \times n$ times as above. Fractions of the regio- and stereosequences based on the Markov chain are also listed in Table S3 (Supporting Information).

In accordance with the stereo- and regiosequences of the PPC chains thus generated, the super generator matrices $H_{ij}^p$'s...
(α = R or S and β = O or A)\(^{23}\) were chosen, arranged, and multiplied sequentially to yield the configurational properties and thermodynamic quantities for the individual chains. The final outcomes were the averages over all of the \( n_c \) chains. In our previous study on poly(lactide)s,\(^{70}\) fluctuations in data resulting from the stochastic processes were found to decrease with increasing number (\( x \times n_c \)) of trials. When \( x = n_c = 300 \), the accuracy and reproducibility were fully satisfactory. Therefore, this study has generally employed \( x = n_c = 300 \), except when the data on the infinite chain (\( x = \infty \)) were determined from the extrapolation of the datum versus \( x^{-1} \) plot. Then, the \( x \) and \( n_c \) values were set as 100 ≤ \( x \) ≤ 300 and \( n_c = 300 \).

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00964.

Statistical weight matrices of PEC; statistical weight matrices of PPC; geometrical parameters of PEC; geometrical parameters of PPC; and fractions of regio- and stereosequences in Bernoulli and Markov statistics for PPC (PDF)

## AUTHOR INFORMATION

Corresponding Author

*E-mail: sasanuma@faculty.chiba-u.jp. Phone: +81 (0)43 290 3394. Fax: +81 (0)43 290 3394.

Notes

The authors declare no competing financial interest.

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