Polymer 55 (2014) 1901–1911

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

# Configurational statistics of poly(L-lactide) and poly(DL-lactide) chains

Yuji Sasanuma*, Daichi Touge

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

## ARTICLE INFO

*Article history:*
Received 30 December 2013
Received in revised form
28 January 2014
Accepted 29 January 2014
Available online 11 February 2014

*Keywords:*
Poly(lactide)
Ab initio statistical mechanics
Configurational properties

## ABSTRACT

Conformational characteristics of poly(lactide)s have been investigated by density functional theory and ab initio molecular orbital (MO) calculations and NMR experiments on model compounds. Characteristic ratios, configurational entropies, and internal energies of poly(L-lactide) and poly(DL-lactide), whose stereosequences were generated by Bernoulli and Markov stochastic processes, were calculated under the refined rotational isomeric state scheme with conformational energies and geometrical parameters derived from the MO calculations. In terms of the conformational characteristics thus revealed, we have elucidated the reason why unperturbed chain dimensions determined experimentally for poly(L-lactide) are scattered considerably and, furthermore, discussed crystallization and crystal structures of poly(L-lactide) and molecular characteristics of poly(DL-lactide) synthesized from *rac*-lactide with stereospecific polymerization catalysts.

## 1. Introduction

Poly(lactic acid) is a biodegradable thermoplastic polyester, which has been produced from renewable sources and molded into a variety of articles for daily use, such as films, wrappings, laminates, and bottles. Lactic acid is produced in part by fermentation of corn; accordingly, we can reap a benefit of fixation of carbon dioxide via maize growth on farms. The sustainable polymer has been manufactured by direct polycondensation of lactic acid in azeotropic solutions or by ring-opening polymerization of lactide, a cyclic dimer of lactic acid [1].

Lactide includes two asymmetric carbon atoms; L-lactide has two (*S*)-chiral centers, and D-lactide contains two (*R*)-enantiomers (see Fig. 1). A racemate of L- and D-lactides is designated as *rac*-lactide. In this paper, $x$ represents the degree of polymerization in lactide unit, and hence $2x$ corresponds to the number of lactic acid units (see Fig. 2). The DD and LL diads are designated as *iso*, and DL and LD as *syn*.

Configurational properties of poly(L-lactide) have long been investigated. By static light scattering and viscosity measurements, Tonelli and Flory determined the characteristic ratio ($<r^2>_0/nl^2$) of poly(L-lactide) dissolved in bromobenzene at 85 °C as 4.4 ± 0.4 [2]. It should be noted that their original $<r^2>_0/nl^2$ value (2.0 ± 0.2) has been reevaluated here with three bond lengths (1.360, 1.436, and 1.532 Å) that we have determined (see Table 6), because they used a virtual bond to calculate the chain dimension. The temperature coefficient $d \ln<r^2>_0/dT$, was reported to be $-5 \times 10^{-3}$ K$^{-1}$. In as much as bromobenzene at 85 °C is a good solvent for poly(L-lactide), the expansion coefficient $\alpha$ was estimated with the Orofino–Flory equation [3] to evaluate the unperturbed dimension according to $<r^2>_0 = <r^2>/\alpha^2$, where $<r^2>$ is the observed mean square end-to-end distance. Brant, Tonelli, and Flory exactly reproduced the experimental $<r^2>_0/nl^2$ value by the rotational isomeric state (RIS) calculations with conformational energies extracted from a two-dimensional energy map [4].

After the pioneering work of Flory et al., a number of experiments have been conducted to determine unperturbed chain dimensions of poly(lactide)s. The representative examples are listed in Table 1, where the $<r^2>_0/nl^2$ values have been recalculated with our bond lengths. These data, measured by different methods and analyzed through elaborate procedures, are scattered to a considerable extent ($<r^2>_0/nl^2 \approx 6$–14) and larger than that (4.4 ± 0.4) of Flory et al. One of our purposes here is to theoretically reveal the reason for the data dispersion and show polymer scientists and engineers how to comprehendcharacteristic features of poly(lactide)s.

Polymerization of L-lactide yields isotactic poly(L-lactide), which melts around 170–180 °C (melting point, $T_m$). Equimolar

---

* Corresponding author. Tel./fax: +81 43 290 3394.
*E-mail address:* sasanuma@faculty.chiba-u.jp (Y. Sasanuma).

http://dx.doi.org/10.1016/j.polymer.2014.01.059
0032-3861/© 2014 Elsevier Ltd. All rights reserved.

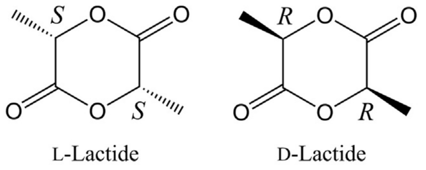

**Fig. 1.** L-Lactide and D-lactide. *rac*-Lactide is a racemate of these two enantiomers.

mixtures of poly(L-lactide) and poly(D-lactide) crystallize to form stereocomplexes of $T_m$ = 220–230 °C [5]. *rac*-Lactide is polymerized to include various stereosequences, depending on catalyst (initiator). For example, tin (II) octoate [6] and lithium *tert*-butoxide [7] catalyze the polymerization to yield *syn*-rich poly(DL-lactide)s. Single-site metal alkoxide catalysts generate different configurational sequences in the resulting poly(DL-lactide) chains [8,9]. As an example, a racemate of chiral aluminum alkoxides yields *iso*-rich stereoblock poly(DL-lactide) [10,11]. Furthermore, a variety of aluminum and non-aluminum complexes have been developed for polymerization of *rac*-lactide [12–20]. Another purpose of this study is to theoretically characterize poly(lactide)s synthesized from *rac*-lactide as well as L-lactide with different catalysts.

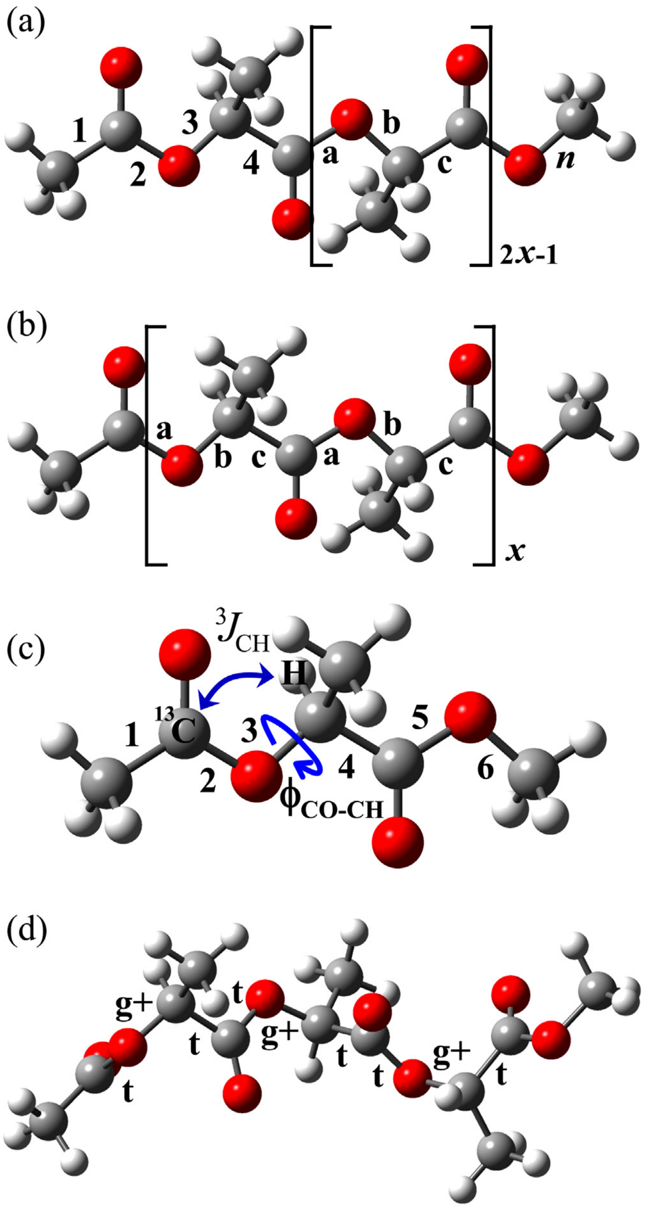

**Fig. 2.** (a) Poly((*S*)-lactic acid), (b) poly(L-lactide), (c) (*S*)-methyl 2-acetoxypropanoate (designated as monomer), and (d) 1-methoxy-1-oxopropan-2-yl 2-((2-acetoxypropanoyl)oxy)propanoate (timer) depicted in the tg$^+$ttg$^+$ttg$^+$t conformation of the *SSS* form. The bonds are numbered or designated as indicated, *x* is the degree of polymerization in lactide unit. $^3J_{CH}$ is the vicinal coupling constant between the $^{13}$C-labeled carbonyl carbon and methine proton of monomer–$^{13}$C, and $\phi_{CO-CH}$ is the dihedral angle used in eqs. (7)–(9).

In this study, first, density functional theory and ab initio molecular orbital (MO) calculations and NMR experiments on a monomeric model of poly(L-lactide) were carried out, and the theoretical and experimental data were compared to check the reliability of the MO computations. Next, the $\langle r^2\rangle_0/nl^2$ values of poly(L-lactide) and poly(DL-lactide)s, whose configurational sequences were generated by Bernoulli trials, were calculated under the refined RIS scheme [21] using conformational free energies and geometrical parameters derived from trimeric model compounds of lactic acid and compared with experimental $\langle r^2\rangle_0/nl^2$'s to fulfill the first purpose and select the MO energies suitable for poly(lactide)s. Stereosequences of poly(DL-lactide)s were generated by a Markov process so as to match *iso*/*syn* ratios of the actual polymers synthesized from *rac*-lactide with stereospecific polymerization catalysts, and their chain dimensions and thermodynamic quantities were calculated under the refined RIS scheme to elucidate their molecular characteristics and physical properties, i.e., to achieve the second purpose. Herein the methodologies are explained, and the results are described and discussed in detail.

## 2. Materials and methods

### 2.1. MO calculations on model compounds

Density functional theory and ab initio MO calculations were carried out with the Gaussian09 program [29] installed on an HPC Systems 5000-Z800 computer or a Hitachi SR16000 server in the Institute of Management and Information Technologies of Chiba University. For each conformer of (*S*)-methyl 2-acetoxypropanoate (referred hereafter to as monomer, see Fig. 2c), its geometrical parameters were fully optimized at the B3LYP/6-311+G(2d,p) level, and its thermochemical parameters at 25 °C and 1 atm were calculated. All self-consistent field calculations were conducted under the tight convergence. With the optimized geometry, the electronic energy was computed at the MP2/6-311+G(2d,p) level. The Gibbs free energy was evaluated at both B3LYP/6-311+G(2d,p) and MP2/6-311+G(2d,p) levels, being given here as the difference from that of the tg$^+$tt conformer and denoted as $\Delta G_k$ (*k*: conformer). Herein, for example, tg$^+$tt expresses that bonds 2, 3, 4, and 5 adopt trans, gauche$^+$, trans, and trans states, respectively (for the bond numbers, see Fig. 2c). Similar calculations were performed for *SSS*, *RRS*, and *RSS* enantiomers of 1-methoxy-1-oxopropan-2-yl 2-((2-acetoxypropanoyl)oxy)propanoate (designated as trimer, Fig. 2d). Then, only the third lactic acid unit underwent conformational changes with the first and second being fixed in tg$^+$t ((*S*)-isomer) or tg$^-$t ((*R*)-isomer), where, for example, tg$^+$t represents that bonds a, b, and c adopt trans, gauche$^+$, and trans states, respectively. The solvent effect on $\Delta G_k$ was evaluated by the integral equation formalism of the polarizable continuum model [30] for the following media: monomer, gas phase and chloroform at 25 °C; trimer, gas and chloroform environments at 25 and 207 °C (equilibrium melting point, $T_m^0$, of poly(L-lactide)) [31,32], and bromobenzene at 85 °C. Bond lengths, bond angles, and dihedral angles for the refined RIS calculations on poly(L-lactide) and poly(DL-lactide)s were chosen from the optimized geometrical parameters of the trimers (see Table S1, Supplementary Data). In our previous