Macromolecules
NOTE

Macromolecules **2009**, *42*, 4907–4909 **4907**
DOI: 10.1021/ma900760z

A Direct Function Relationship between Isotacticity and Melting Temperature of Multiblock Stereocopolymer Poly(*rac*-lactide)

Nobuyoshi Nomura,* Jun Hasegawa, and Ryohei Ishii

Laboratory of Polymer Chemistry, Graduate School of Bioagricultural Sciences, E1-1(300),
Nagoya University, Nagoya 464-8601, Japan

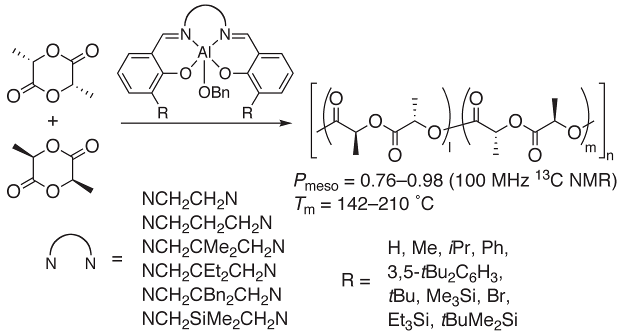
Received April 8, 2009; Revised Manuscript Received May 21, 2009

The stereoselective ring-opening polymerization (ROP) of racemic lactide (*rac*-LA) has been one of the topics in industry as well as in academia[1] because the poly(*rac*-LA) with a high isotacticity has a melting temperature higher than that of the commercially available homochiral poly(L-lactide) (poly(L-LA), T_m ~170 °C[2]) and could be a practical material superior to the homochiral poly (L-LA).[3] Various catalysts, such as homochiral,[4] racemic,[5−7] and achiral[8] metal complexes, and also some organic carbenes,[9] have been reported for the isotactic polymerization of *rac*-LA, and we have studied the achiral salen− and homosalen−Al complexes with various substituents[10−12] (Scheme 1). Throughout our systematic experiments, we obtained a number of crystalline isotactic multiblock stereocopolymers with a wide range of isotactic selectivities (P_{meso}'s). It was generally observed that the melting temperature increased as the stereoselectivity of the poly(*rac*-LA) increased. Therefore, a mathematical relationship between P_{meso} and T_m was theorized. We now report the direct function relationship between P_{meso} and T_m.

The 35 coordinates[13] for the isotactic poly(*rac*-LA) with P_{meso}[14] by 100 MHz ^{13}C NMR along with the *x*-axis and T_m[15] along with the *y*-axis, (P_{meso}, T_m), were plotted, and there seemed to be a linear relationship between P_{meso} and T_m (the absolute coefficient, $R^2 = 0.95_3$). One of the DSC traces is shown in Figure 1 (T_m=210 °C). For more accurate P_{meso} data than ones from the 100 MHz ^{13}C NMR (Figure 2a), we carefully reanalyzed the P_{meso} values of 30 samples by 150 MHz ^{13}C NMR under the identical conditions that included a substantial measuring time (12 h 20 min for each sample).[16] The minor *mrm* peak at 69.15 ppm of the 150 MHz ^{13}C NMR (Figure 2b) appeared more clearly than the one of the 100 MHz ^{13}C NMR (Figure 2a). The 30 coordinates of (P_{meso}, T_m) are plotted in Figure 3, and some of them were overlapped. The absolute coefficient, R^2=0.97$_2$, was reasonably improved, and the linear relationship between P_{meso} and T_m became more reliable when compared to the coordinates of the P_{meso} data from the 100 MHz ^{13}C NMR ($R^2 = 0.95_3$ for all 35 samples; R^2=0.94$_5$ for the 30 samples).

The absolute coefficient $R^2 = 0.97_2$ indicates that there is a direct function relationship between P_{meso} and T_m for poly(*rac*-LA) in the ranges of $0.78 \leq T_m \leq 0.98$ and $4700 \leq M_n \leq 59\,500$. It is generally well-known that various factors influence the T_m of polymer molecules,[17] e.g., the molar mass up to a certain degree of polymerization, i.e., the role played by chain ends with a low degree of polymerization, structural irregularities, various impurities, etc. Technically, the nucleation and annealing conditions are also important. All of the poly(*rac*-LA)s in this study had been purified and measured under similar conditions after they were synthesized via the ROP of *rac*-LA. Therefore, the major parameter that strongly influences the T_m except for the structural irregularities would be the molecular weight. We analyzed 30 samples of isotactic poly(*rac*-LA) in the range of $4700 \leq M_n \leq 59\,500$, but the linear relationship between P_{meso} and T_m was not significantly influenced by the difference in M_n. It is reasoned that the T_m of the stereocomplex poly(*rac*-LA) is highly dependent on P_{meso}, and the effect of the molecular weight is much lower than the effect of P_{meso}. At present, we cannot offer a theory or model to explain this relationship. A similar observation on the structure−T_m correlations of isotactic polypropylene has been reported,[18] and it might be a guide.

Scheme 1. Stereoselective ROP of Racemic Lactide by Achiral Salen− and Homosalen−Al Complexes



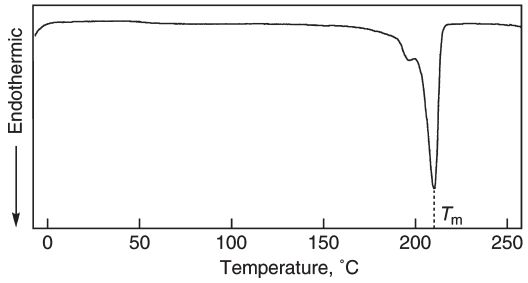


Figure 1. One of the DSC traces to determine a T_m value.

There are two ultimate mechanisms for the efficient stereoselective polymerization of *rac*-LA:[19] one is a chain-end control mechanism[20] (CEM), which we examined, and the other is a site control mechanism[21] (SCM) using a racemic complex with a chiral environment. In this study, P_{meso} has been used for the stereoselectivity of the isotactic poly(*rac*-LA) via the CEM, and P_{iso} is used for the stereoselectivity via the SCM in contrast to the

---

*Corresponding author. E-mail: nnomura@nagoya-u.jp.

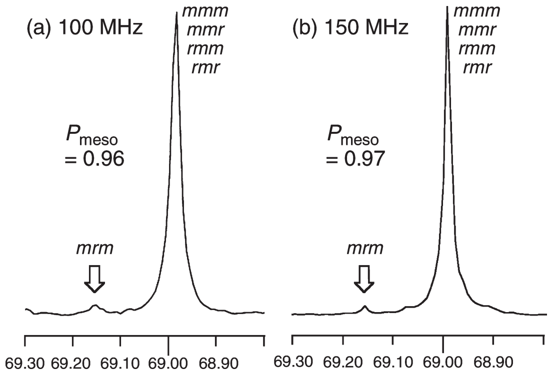


Figure 2. ^{13}C NMR spectra of methine region of the same sample: *m*, *meso* (isotactic diad); *r*, *racemo* (syndiotactic diad).

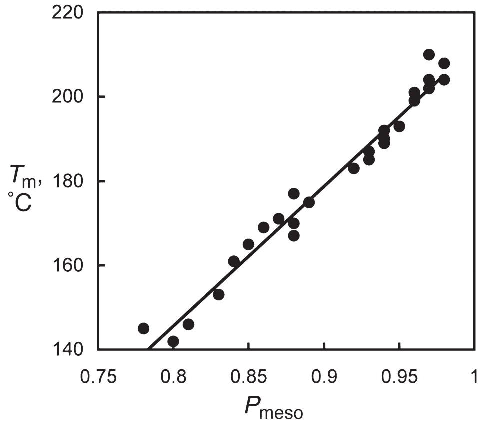
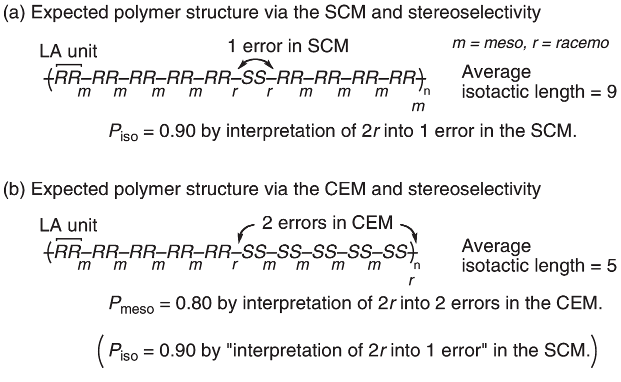


Figure 3. Plots of (P_{meso}, T_m); 30 coordinates after reanalysis (P_{meso} by 150 MHz ^{13}C NMR).

Scheme 2. Stereoselectivities in the SCM and CEM



P_{meso}. Although the SCM process had initially been believed to afford optically active polymer molecules, such as the one shown in Scheme 2a, Coates et al. found that the polymerization of racemic lactide by a racemic complex afforded a multiblock stereocopolymer,[6] which had the same microstructure pattern via the CEM (Scheme 2b). When the stereocopolymer via the SCM is estimated according to its definition, the P_{iso} value is higher than that of P_{meso}. The P_{iso} value via the SCM with a polymer/ligand exchange process may express the selectivity of catalysis but is not related to the isotacticity of the poly(*rac*-LA).[6,22] As a matter of fact, the isotactic length in Scheme 2b does not match with the one in Scheme 2a even for the same P_{iso} value. Therefore, there is no comparison of the P_{iso} value and P_{meso} value when the microstructure pattern of the poly(*rac*-LA) is the same.

In conclusion, we revealed the direct function relationship between P_{meso} and T_m of the multiblock stereocopolymer poly(*rac*-LA) that was synthesized via the CEM in the range of $0.78 \leq P_{meso} \leq 0.98$ and $4700 \leq M_n \leq 59\,500$. Although this is an empirical observation without a theoretical background at present, it indicates that the stereoregularity of poly(*rac*-LA) is a straightforward parameter for the higher order architecture such as lamella thickness, which is well-known to define the T_m values.[23]

Acknowledgment. This paper is dedicated to the memory of the late Professor Tadamichi Hirabayashi (Nagoya Institute of Technology). Part of this work was financially supported by Grant-in-Aid for Scientific Research (C) (18550108 and 21550116). We thank Mr. Yutaka Maeda of the Chemical Instrument Facility, Research Center for Material Science, Nagoya University, for his assistance with the 150 MHz ^{13}C NMR measurements.

Supporting Information Available: Experimentals, all of the sample data, the graph with 35 plots using P_{meso} by 100 MHz ^{13}C NMR, and graphs with 30 plots using P_{meso} by 100 and 150 MHz ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Seppala, J. V.; Korhonen, H.; Kylma, J.; Tuominen, J. In *Biopolymers*; Steinbuechel, A., Doi, Y., Eds.; Wiley-Interscience: Weinheim, 2001; Vol. 3b, pp 327−370. (b) Duda, A.; Penczek, S. In *Biopolymers*; Steinbuechel, A., Doi, Y., Eds.; Wiley-Interscience: Weinheim, 2001, Vol. 3b, pp 371−429. (c) Tsuji, H. In *Biopolymers*; Steinbuechel, A., Doi, Y., Eds.; Wiley-Interscience: Weinheim, 2001, Vol. 4, pp 129−178. (d) Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87. (e) Chiellini, E.; Solaro, R. *Adv. Mater.* **1996**, *8*, 305. (f) Hayashi, T. *Prog. Polym. Sci.* **1994**, *19*, 663.

(2) T_m = 162 °C: Yui, N. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 10, p 7947. T_m=164 °C (M_n = 12 400 by SEC), synthesized in our lab using Al(O*i*Pr)$_3$; T_m = 174 °C (M_n = 59 300 by SEC), synthesized in bulk in our lab, see Table 4 in ref 11. T_m = 180 °C: Södergrrd, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.

(3) The relatively rapid decomposition is a well-known property of PLA when heated above the melting point: Wachsen, O.; Reichert, K. H.; Kruger, R. P.; Much, H.; Schulz, G. *Polym. Degrad. Stab.* **1997**, *55*, 225.

(4) (a) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627. (b) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026.

(5) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552.

(6) (a) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4686. (b) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316.

(7) (a) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4510. (b) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291.

(8) (a) Le Borgne, A.; Vincens, V.; Jouglard, M.; Spassky, N. *Makromol. Chem., Macromol. Symp.* **1993**, *73*, 37. (b) Wisniewski, M.; Le Borgne, A.; Spassky, N. *Macromol. Chem. Phys.* **1997**, *198*, 1227. (c) Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616. (d) Bhaw-Luximon, A.; Jhurry, D.; Spassky, N. *Polym. Bull.* **2000**, *44*, 31. (e) Jhurry, D.; Bhaw-Luximon, A.; Spassky, N. *Macromol. Symp.* **2001**, *175*, 67. (f) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688. (g) Tang, Z.; Chen, X.; Pang, X.; Yang, Y.; Zhang, X.; Jing, X. *Biomacromolecules* **2004**, *5*, 965. (h) Tang, Z.; Chen, X.; Yang, Y.; Pang, X.; Sun, J.; Zhang, X.; Jing, X. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5974. (i) Pang, X.; Chen, X.; Du, H.; Wang, X.; Jing, X. *J. Organomet. Chem.* **2007**, *692*, 5605. (j) Pang, X.; Du, H.; Chen, X.; Wang, X.; Jing, X. *Chem.—Eur. J.* **2008**, *14*, 3126.

(9) (a) Jensen, T. R.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *Chem. Commun.* **2004**, 2504. (b) Dove, A. P.; Li, H.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, 2881.

(10) (a) Nomura, N.; Ishii, R.; Aoi, K.; Akakura, M. *50th SPSJ Symp. Macromol. Polym. Prepr., Jpn.* **2001**, *50*, IIPc003. (b) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (c) Ishii, R.; Nomura, N.; Kondo, T. *Polym. J.* **2004**, *36*, 261.

(11) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433.

(12) Gibson et al. also reported their comprehensive studies of the backbones and substituents on the Al complexes with salen-type ligands: Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343.

(13) See the Supporting Information.

(14) $[mrm]/[mrm + mmm + mmr + rmm + rmr] = (1 - P_{\text{meso}})/2$: (a) Coudane, J.; Ustariz-Peyret, C.; Schwach, G.; Vert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1651. (b) Kasperczyk, J. E. *Macromolecules* **1995**, *28*, 3937.

(15) T_m's were measured by differential scanning calorimetry (DSC) under N_2. In order to provide the same thermal history for all samples, thermal data were obtained after one heating cycle to 230 °C at a heating rate of 10 °C/min, followed by quenching to 0 °C in the DSC. The DSC profiles were recorded at a heating rate of 10 °C/min to 230 °C. The T_m values were taken as the inflection point of the specific heat increment (see Figure 1).

(16) Since we had insufficient sample (less than 30 mg) for five poly(*rac*-LA)s, they were not reanalyzed. The sample conditions for 150 MHz ^{13}C NMR: 30 mg of poly(*rac*-LA), 0.6 mL of $CDCl_3$. The measuring conditions: points, 32 768; frequency, 40 650.41 Hz; scans, 24 576; acquisition time, 0.8061 s; pulsing delay, 1.0000 s; pulse width 1, 6.50 μs for each sample.

(17) Gnanou, Y.; Fontanille, M. *Organic and Physical Chemistry of Polymers*; John Wiley & Sons: Hoboken, NJ, 2008; Chapter 11.3.

(18) There is an excellent report on the structure defects−T_m correlations in isotactic polypropylene: (a) De Rosa, C.; Auriemma, F.; Di Capua, A.; Resconi, L.; Guidotti, S.; Camurati, I.; Nifant'ev, I. E.; Laishevtsev, I. P. *J. Am. Chem. Soc.* **2004**, *126*, 17040. The most important factor affecting the structure and properties of isotactic polypropylene is the isotacticity content: (b) Arranz-Andrés, J.; Peña, B.; Benavente, R.; Pérez, E.; Cerrada, M. L. *Eur. Polym. J.* **2007**, *43*, 2357. The melting relationships relevant to this paper were also reported. For polyethylene single crystals: (c) Wunderlich, B.; Czornyj, G. *Macromolecules* **1977**, *10*, 906 and references therein. For ethylene−alkene copolymers: (d) Crist, B.; Howard, P. R. *Macromolecules* **1999**, *32*, 3057. (e) De Rosa, C.; Auriemma, F.; de Ballesteros, O. R.; Resconi, L.; Camurati, I. *Macromolecules* **2007**, *40*, 6600. We thank one of the reviewers for the information of these important references .

(19) According to Chisholm's studies, the effects of the polymer chain end cannot be ruled out in the SCM: Chisholm, M. H.; Patmore, N. J.; Zhou, Z. *Chem. Commun.* **2005**, 127.

(20) In the CEM mechanism, the precatalyst is achiral. See the mechanistic discussion in ref 11.

(21) In the SCM, the catalyst has a chiral environment constructed by the ligand around the metal center and consistently differentiates L-LA from D-LA, preferentially reacting with one enantiomer. Although each polymer molecule obtained via the SCM is supposed to be optically active, the polymer molecules have stereomultiblock sequences because of polymer/ligand exchanges during the polymerization. See ref 6.

(22) As far as we know, Coates et al. adequately pointed it out in ref 6 and reported the average isotactic length (n) to minimize the difference between the simulation output (P_{iso}=0.98) and actual microstructure (n=11). Unfortunately, it has not been since well acknowledged.

(23) We thank one of the reviewers, who kindly pointed it out.