

Enhanced stereocomplex formation of high-molecular-weight polylactides by gelation in an ionic liquid

Jie Zhu, Bing Na,* Ruihua Lv and Chun Li

Abstract

It is still a challenge to achieve a high degree of stereocomplexation in enantiomeric polylactides with high molecular weight. This study demonstrates that gelation of enantiomeric polylactides in an ionic liquid, a non-volatile solvent, is a facile route to overcome this problem. The presence of the ionic liquid enhances the molecular mobility and mutual diffusion and thus to a large extent eliminates the kinetic barrier for stereocomplex formation. The gelation and stereocomplex formation in the ionic liquid may provide a new opportunity for the application of polylactides as scaffolds with high thermal stability in tissue engineering.

© 2013 Society of Chemical Industry

Keywords: stereocomplex; polylactide; gelation; ionic liquid

INTRODUCTION

Stereocomplexation between enantiomeric polylactides, namely poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), is a promising route for improving the thermal stability and hydrolysis resistance of polylactides.^{1–9} The side-by-side dense packing between enantiomeric chains in the unit cell, as a result of strong intermolecular interactions, significantly enhances the melting point of the stereocomplex, higher by about 50 °C than that of homocrystals formed by either PLLA or PDLA.^{10,11} Thus, from the viewpoint of thermodynamics, stereocomplex formation could be favored over homocrystallization. However, a high kinetic barrier, i.e. low molecular interdiffusion, prevents stereocomplex formation, especially in enantiomeric polylactides with high molecular weight.¹²

Because high molecular weight is indispensable for superior mechanical properties, many attempts have been made to develop methods for achieving a high degree of stereocomplexation from enantiomeric polylactides with high molecular weight. Annealing at temperatures between the melting points of stereocomplex and homocrystal is an effective way to transform homocrystal to stereocomplex.^{13–16} Meanwhile, melt mixing at relatively low temperatures also favors stereocomplex formation by suppressing homocrystallization.¹⁷ In addition, use of a supercritical fluid and repeated casting can assist stereocomplex formation at the expense of homocrystal formation.^{18,19}

Ionic liquids are a type of organic salts with low melting point and negligible vapor pressure. As non-volatile solvents, ionic liquids have been extensively used in fabricating novel materials.^{20–23} In the study reported here, a high degree of stereocomplexation was for the first time achieved by gelation of enantiomeric polylactides with high molecular weight in an ionic liquid. It is believed that the kinetic barrier is to a large extent eliminated upon gelation in

the ionic liquid where enhanced molecular mobility and mutual diffusion are expected.

EXPERIMENTAL

Materials and sample preparation

Two kinds of PLLAs, purchased from Natureworks, USA, were used. One had M_n and M_w of 56 and 74 kg mol⁻¹, respectively (PLLA-L); the other had M_n and M_w of 123 and 210 kg mol⁻¹, respectively (PLLA-H). PDLA, having M_n and M_w of 254 and 411 kg mol⁻¹, respectively, was provided by Changchun Sinobiomaterials Co. Ltd, China. The ionic liquid used, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([EMIM]NTf₂), was obtained from Lanzhou Institute of Chemical Physics, China, and used as received. Figure 1 shows the molecular structure of the ionic liquid. Of note, the ionic liquid is viscous at room temperature because of its low melting point. PLLA and PDLA were directly dissolved in the ionic liquid at 210 °C under stirring to form a transparent solution with a total polymer concentration of 0.2 g mL⁻¹; the mass ratio of PLLA and PDLA was 50:50. Upon cooling to room temperature the solution underwent gelation and thus an opaque gel was obtained (referred to as wet gel), as shown in Fig. 2(a). After removal of the ionic liquid by rinsing with methanol, the wet gel was transformed to a dry gel. For comparison, chloroform was used as a conventional

* Correspondence to: Bing Na, Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, School of Biology, Chemistry and Material Science, East China Institute of Technology, Nanchang 330013 People's Republic of China. E-mail: bna@ecit.edu.cn

Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, School of Biology, Chemistry and Material Science, East China Institute of Technology, Nanchang 330013, People's Republic of China

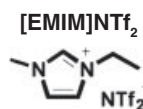


Figure 1. Molecular structure of ionic liquid [EMIM]NTf₂.

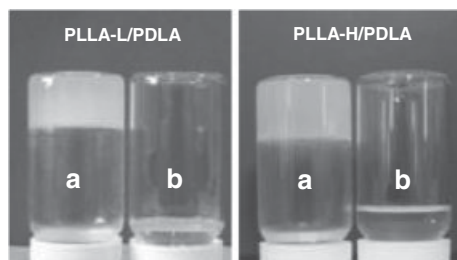


Figure 2. Optical photographs of PLLA-L/PDLA and PLLA-H/PDLA solution at room temperature with (a) the ionic liquid and (b) chloroform as solvent.

solvent to generate a PLLA/PDLA solution with the same concentration and mass ratio at room temperature. This solution was stable and no gelation was observed at room temperature (Fig. 2(b)). To obtain films, the solution was cast on a glass plate to evaporate the chloroform.

Characterization

DSC measurements were conducted at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere using a PerkinElmer Pyris-1 DSC instrument. Fourier transform infrared (FTIR) spectra were measured using a Thermo Nicolet FTIR spectrometer with a resolution of 4 cm⁻¹. To obtain structural changes with temperature, a hot stage was coupled with the FTIR spectrometer in its sample compartment. XRD profiles were obtained using an X-ray diffractometer equipped with an X-ray generator and a goniometer at room temperature. The X-rays were generated at 35 kV and 60 mA, and the wavelength of the monochromated X-rays was 0.154 nm.

RESULTS AND DISCUSSION

Figure 3 shows DSC heating traces of wet gel, dry gel and cast film of PLLA-L/PDLA blends. Two main thermal transitions, in the temperature range of about 160–180 and 200–220 °C, are observed for the cast film. These correspond to the melting of homocrystal and stereocomplex, respectively, when their thermal stability is considered.^{12,24} Compared to that of homocrystal, the endotherm of stereocomplex is relatively insignificant, suggesting that only a part of PLLA-L and PDLA takes part in the stereocomplexation during solution casting. This is a common observation in the solution casting of PLLA/PDLA blends with high molecular weight.^{17,19} However, this situation is totally changed upon gelation of PLLA-L and PDLA in the ionic liquid. For the dry gel, the melting of stereocomplex in the temperature range of about 200–220 °C becomes overwhelming, whereas the endotherm related to homocrystal nearly disappears. This means that gelation in the ionic liquid is a promising route for achieving a high degree of stereocomplexation in the polylactides. The relatively low melting temperature exhibited by the wet gel

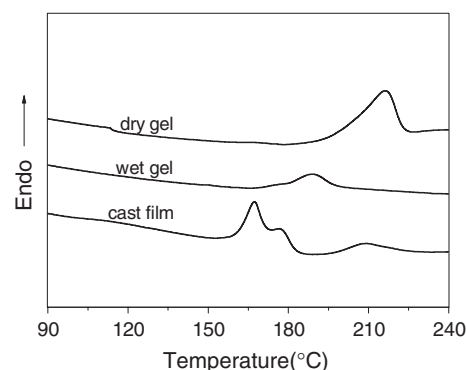


Figure 3. DSC heating traces of wet gel, dry gel and cast film of PLLA-L/PDLA blends.

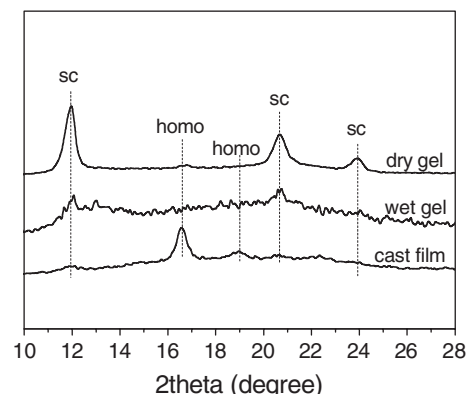


Figure 4. Room temperature XRD profiles of wet gel, dry gel and cast film of PLLA-L/PDLA blends. The labels 'sc' and 'homo' represent stereocomplex and homocrystal, respectively.

is because the presence of the ionic liquid suppresses the melting point of stereocomplex, similar to that observed for other polymer systems containing ionic liquids.²⁵

To further confirm stereocomplex formation in the ionic liquid, XRD and FTIR measurements were conducted. Figure 4 shows the XRD profiles of wet gel, dry gel and cast film of PLLA-L/PDLA blends. The diffractions at 2θ of around 12°, 21° and 24° are assigned to the (110), (300)/(030) and (220) planes of stereocomplex, respectively; the homocrystal has characteristic diffractions at 2θ of about 16.5° and 19°, corresponding to the (200)/(110) and (203) planes, respectively.^{1,26} Stereocomplex formation in the wet and dry gels is marked, whereas homocrystal prevails in the solution-cast film. Of note, the weak diffractions from the wet gel are mostly related to the low concentration of polylactides in the gel. In addition, FTIR spectroscopy is a powerful tool for distinguishing stereocomplex from homocrystal, as shown in Fig. 5. The absorption bands at 921 and 908 cm⁻¹ are assigned to the 10₃ helix of homocrystal and the 3₁ helix of stereocomplex, respectively.^{27–29} Both wet and dry gels of PLLA-L/PDLA blends show remarked absorption at 908 cm⁻¹, whereas the absorption at 921 cm⁻¹ is nearly absent (Fig. 5(a)). This suggests that stereocomplex formation occurs during gelation and has little to do with the rinsing with methanol. In contrast, formation of stereocomplex in the films cast from chloroform solution is less significant, and homocrystallization is dominant. The degree of stereocomplexation, deduced from the relative peak area of the 908 cm⁻¹ band, is 97, 96 and 15% for dry gel, wet gel and cast film of PLLA-L/PDLA blends, respectively.

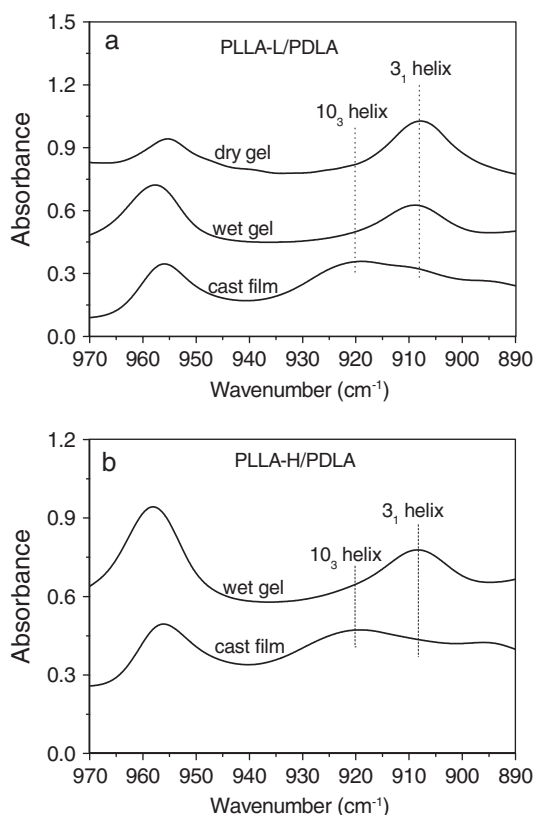


Figure 5. Room temperature FTIR spectra of gel and cast film of (a) PLLA-L/PDLA and (b) PLLA-H/PDLA blends. The spectra are vertically shifted for clarity.

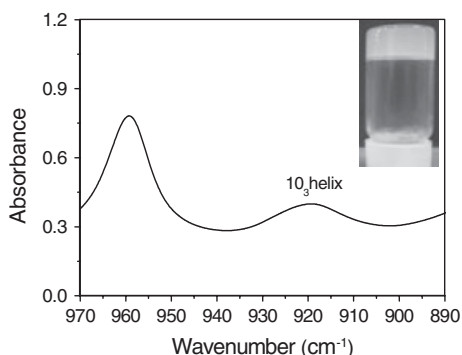


Figure 6. FTIR spectrum and optical photograph of PLLA-L solution with ionic liquid as solvent at room temperature.

Similar results are also observed for PLLA-H/PDLA blends (Fig. 5(b)); the degree of stereocomplexation is 96 and 8% for wet gel and cast film, respectively. Again, this confirms that gelation in the ionic liquid benefits stereocomplex formation even for enantiomeric polylactides with extremely high molecular weight.

The results discussed above clearly demonstrate that the enantiomeric polylactides with high molecular weight can attract each other to yield a high degree of stereocomplexation in the ionic liquid. In contrast, in chloroform no gel is produced and no stereocomplexation occurs during the experimental period; only in the cast film is some amount of stereocomplex induced after evaporation of chloroform. This difference could be related to the distinctly different solubility of the polylactides in ionic liquid

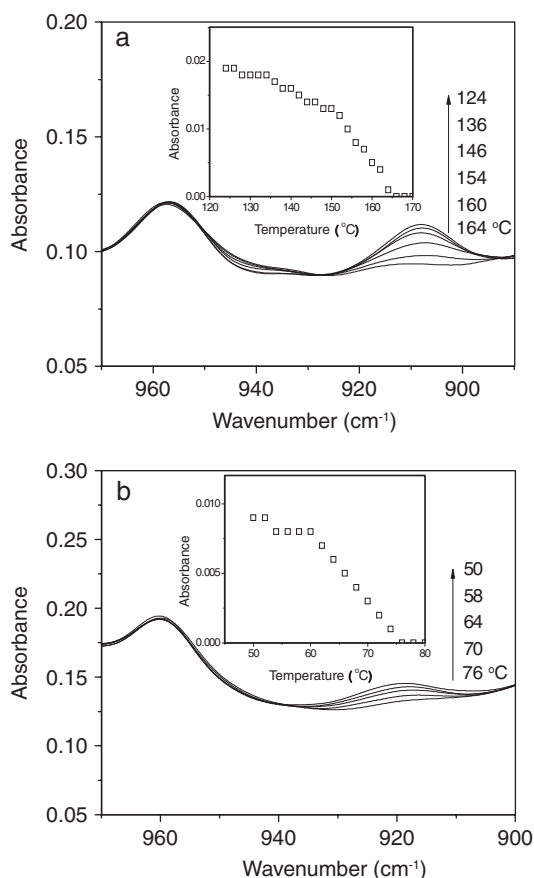


Figure 7. Temperature-dependent FTIR spectra upon cooling of (a) PLLA-L/PDLA blend and (b) PLLA-L in ionic liquid. Insets: change in absorbance of (a) 908 cm^{-1} band and (b) 921 cm^{-1} band with temperature.

and chloroform. Chloroform is a good solvent for polylactides and a clear solution can be prepared at room temperature. But, the solubility of the polylactides in the ionic liquid is relatively low, and they are only dissolved at high temperatures. Of note, the solubility parameter is 9.3 and 13.6 (cal cm^{-3})^{1/2} for chloroform and the ionic liquid [EMIM]NTf₂, respectively.³⁰ Upon cooling, polylactides tend to crystallize and thus gelation is induced due to the construction of a three-dimensional network by crystallites. However, gelation as well as crystallization are also observed for single PLLA (PLLA-L or PLLA-H) in the ionic liquid. Figure 6 shows the results for PLLA-L in the ionic liquid; the concentration of PLLA-L in the ionic liquid is 0.2 g mL^{-1} . Thus, low solubility in the ionic liquid cannot account for the stereocomplex formation of enantiomeric polylactides, different from that observed for isotactic and syndiotactic poly(methyl methacrylate)s in ionic liquids.³¹

The presence of the ionic liquid could enhance the molecular mobility and mutual diffusion of the enantiomeric polylactides, and thus eliminate the kinetic barrier for stereocomplex formation to a large extent. In such a sense, stereocomplexation should take over the crystallization process when thermodynamic factors are considered. To confirm this, *in situ* FTIR measurements of the wet gel of PLLA-L and PLLA-L/PDLA blend upon cooling were carried out. The wet gel was first heated to 210 °C and then cooled at 5 °C min^{-1} . As shown in Fig. 7(a), stereocomplex formation, characterized by the 908 cm^{-1} band, in the PLLA-L/PDLA blend appears around 164 °C and becomes almost complete before 120 °C. As a comparison, homocrystallization of PLLA-L in the

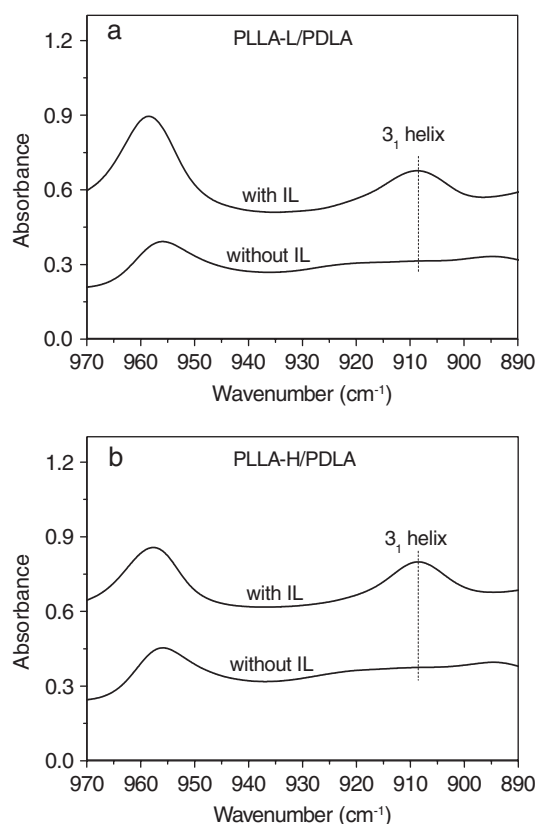


Figure 8. Room temperature FTIR spectra of (a) PLLA-L/PDLA and (b) PLLA-H/PDLA blends with and without ionic liquid (IL) after cooling from 230 °C at 20 °C min⁻¹. The spectra are vertically shifted for clarity.

ionic liquid occurs only at around 76 °C, as demonstrated by the absorbance change of the 921 cm⁻¹ band (Fig. 7(b)). This means that the driving force for stereocomplexation in the ionic liquid is larger than that for homocrystallization, consistent with the thermal stability of crystals.

The ionic liquid is non-volatile and thermally stable, which benefits stereocomplexation and gelation thermoreversibility. Above the melting point of stereocomplex, the gel disappears, resulting in homogenous and stable solution. Upon cooling, gelation as well as stereocomplexation are induced again. Due to the enhanced molecular mobility and mutual diffusion, stereocomplex formation takes over the gelation process even at a cooling rate of 20 °C min⁻¹, as evident from the FTIR results in Fig. 8. The characteristic 908 cm⁻¹ band of stereocomplex prevails in both PLLA-L/PDLA and PLLA-H/PDLA blends with the ionic liquid. As a comparison, without the ionic liquid crystallization from bulk is significantly suppressed due to limited molecular mobility; and little stereocomplex formation is observed in either PLLA-L/PDLA or PLLA-H/PDLA blends. These results further confirm that the enhanced molecular mobility and mutual diffusion caused by the ionic liquid contributes to stereocomplex formation of enantiomeric polylactides with high molecular weight.

CONCLUSIONS

A high degree of stereocomplexation is achieved by gelation of enantiomeric polylactides with high molecular weight in the ionic liquid. In contrast, in chloroform no gelation and

stereocomplexation are observed; only in the cast films is some stereocomplex induced with evaporation of chloroform. The overwhelming stereocomplex formation in the ionic liquid is a thermodynamically controlled event, and the kinetic barrier for molecular interdiffusion is eliminated to a large extent. In addition, gelation as well as stereocomplex formation in the ionic liquid are thermoreversible, which facilitates the high-temperature processing and low-temperature application of the gel.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (nos. 21004010, 21364001), the Program for Young Scientists of Jiangxi Province (no. 20112BCB23023) and the Major Program of Natural Science Foundation of Jiangxi, China (No. 20133ACB21006).

REFERENCES

- Ikada Y, Jamshidi K, Tsuji H and Hyon SH, *Macromolecules* **20**:904–906 (1987).
- Wang X and Prud'homme RE, *Macromol Chem Phys* **212**:691–698 (2011).
- Furuhashi Y and Yoshie N, *Polym Int* **61**:301–306 (2012).
- Andersson SR, Hakkarainen M, Inkinen S, Södergård A and Albertsson AC, *Biomacromolecules* **11**:1067–1073 (2010).
- Anderson KS and Hillmyer MA, *Polymer* **47**:2030–2035 (2006).
- Yamane H and Sasai K, *Polymer* **44**:2569–2575 (2003).
- Brochu S, Prud'homme RE, Barakat I and Jérôme R, *Macromolecules* **28**:5230–5239 (1995).
- He Y, Xu Y, Wei J, Fan Z and Li S, *Polymer* **49**:5670–5675 (2008).
- Purnama P and Kim SH, *Polym Int* **61**:939–942 (2012).
- Brizzolara D, Cantow HJ, Diederichs K, Keller E and Domb AJ, *Macromolecules* **29**:191–197 (1996).
- Uehara H, Karaki Y, Wada S and Yamanobe T, *ACS Appl Mater Interfaces* **2**:2707–2710 (2010).
- Tsuji H, *Macromol Biosci* **5**:569–597 (2005).
- Furuhashi Y, Kimura Y, Yoshie N and Yamane H, *Polymer* **47**:5965–5972 (2006).
- Fujita M, Sawayanagi T, Abe H, Tanaka T, Iwata T, Ito K et al., *Macromolecules* **41**:2852–2858 (2008).
- Zhang J, Tashiro K, Tsuji H and Domb AJ, *Macromolecules* **40**:1049–1054 (2007).
- Xiong Z, Liu G, Zhang X, Wen T, de Vos S, Joiziasse C et al., *Polymer* **54**:964–971 (2013).
- Bao RY, Yang W, Jiang WR, Liu ZY, Xie BH, Yang MB et al., *Polymer* **53**:5449–5454 (2012).
- Purnama P and Kim SH, *Macromolecules* **43**:1137–1142 (2010).
- Tsuji H and Yamamoto S, *Macromol Mater Eng* **296**:583–589 (2011).
- Likozar B, *Soft Matter* **7**:970–977 (2011).
- Li J, Ma W, Song L, Niu Z, Cai L, Zeng Q et al., *Nano Lett* **11**:4636–4641 (2011).
- He L, Sun J, Wang X, Wang C, Song R and Hao Y, *Polym Int* **62**:638–646 (2013).
- He Y and Lodge TP, *Macromolecules* **41**:167–174 (2008).
- Sun J, Shao J, Huang S, Zhang B, Li G, Wang X et al., *Mater Lett* **89**:169–171 (2012).
- Jansen JC, Friess K, Clarizia G, Schauer J and Izák P, *Macromolecules* **44**:39–45 (2011).
- Sun J, Yu H, Zhuang X, Chen X and Jing X, *J Phys Chem B* **115**:2864–2869 (2011).
- Zhang J, Sato H, Tsuji H, Noda I and Ozaki Y, *Macromolecules* **38**:1822–1828 (2005).
- Na B, Tian N, Lv R, Li Z, Xu W and Fu Q, *Polymer* **51**:563–567 (2010).
- Lv R, Na B, Li Z, Zou S, Tian N, Chen F et al., *J Macromol Sci Phys* **50**:2042–2049 (2011).
- Ueki T and Watanabe M, *Bull Chem Soc Jpn* **85**:33–50 (2012).
- Kawauchi T, Kumaki J, Okoshi K and Yashima E, *Macromolecules* **38**:9155–9160 (2005).