Supplementary Material (ESI) for Chemical Communications
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Stereoselective polymerization of rac- and meso-lactide catalyzed by a sterically encumbered N-heterocyclic carbene

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Experimental

General Methods and Materials. All reactions were performed under an inert atmosphere, using either standard Schlenk techniques or an MBraun glovebox. All solvents and reagents were obtained from commercial sources and used as received unless otherwise stated. Pentane, dichloromethane, tetrahydrofuran and toluene were passed through purification columns. Deuterated solvents (all 99 atom %D) were purchased from Cambridge Isotope Laboratories, dried over calcium hydride, distilled under vacuum, and stored under nitrogen. D,L-Lactide (rac-lactide) was purchased from Purac and purified by recrystallization from toluene. meso-Lactide was prepared based on a literature procedure.1 1,3-dimesitylimidazol-2-ylidene (IMes) was prepared as previously described.2

Characterization. 1H NMR spectra were recorded in CDCl3 with a Bruker Avance 400 (400 MHz) spectrometer with the solvent proton signal as an internal standard. 13C NMR spectra were recorded at 100 MHz on a Bruker Avance 400 spectrometer with the solvent carbon signal as internal standard. Gel permeation chromatography (GPC) was carried out on a Waters chromatography instrument equipped with four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 105, 106) with THF as a solvent and a Waters 410 differential refractometer as detector. Polystyrene samples of known molecular weight were used as calibration standards. Differential scanning calorimetry (DSC) was performed using a TA Differential Scanning
Calorimeter 1000 that was calibrated using high purity indium at a heating rate of 10 °C/min. Melting points were determined from the second scan following slow cooling (to remove the influence of thermal history) at a heating rate of 10 °C/min.

**General Polymerization Procedure.** Glassware used for polymerizations was oven or flame-dried, then oven dried for a minimum of 3 h. A reaction flask was charged in the glovebox with rac-lactide (100 mg, 0.7 mmol), 1-pyrenebutanol (2.06 mg, 7.0 µmol), 1.8 mL of dry CH₂Cl₂ and a magnetic stirbar, then brought out of the glovebox and immersed in a temperature-controlled bath at the desired temperature. A solution of 1 (3.2 mg, 7.0 µmol) in 0.2 mL CH₂Cl₂ was prepared in the glovebox and then removed from the glove box and quickly injected into the rapidly stirring flask using a gas-tight syringe equipped with a spraying needle. After an appropriate time, the reaction mixture was poured into pentane to precipitate the polymer. Excess pentane was removed by decantation and the polymer mixture was dried under vacuum prior to characterization by GPC and ¹H NMR spectroscopy.

**Synthesis of 1.**

1,4-Bis(2,4,6-trimethylphenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene. In a dry 1 L round bottom flask, benzil (5 g, 23.8 mmol) and 2,4,6-trimethylaniline (25.7 g, 190 mmol) were dissolved in 700 mL toluene. TiCl₄ (3.4 mL) was then added and the solution was stirred at 100 °C overnight. H₂O was added to quench the reaction, the toluene layer was next separated, dried over MgSO₄ and filtered. The solvent was removed under vacuum to yield yellow oil. The oil was then purified by column chromatography (silica/CH₂Cl₂) and recrystallization in ethanol (9.5 g, 90% yield). ¹H NMR (CDCl₃, 23 °C, 400 MHz): δ 2.247 (s, 12 H, ortho-CH₃, isomer 1), 2.288 (s, 12 H, ortho-CH₃, isomer 2), 2.598 (s, 6 H, para-CH₃, isomer 1), 2.648 (s, 6 H, para-CH₃, isomer 2), 7.091-7.986 (m, arom), ¹³C NMR (CDCl₃, 23 °C, 100 MHz): δ 18.714 (ortho-CH₃), 19.089 (ortho-CH₃), 20.802 (para-CH₃), 20.932 (para-CH₃), 125.899, 126.780, 127.769, 128.243, 128.502, 128.858, 128.999, 129.148, 129.979, 131.252, 132.882, 135.405, 144.962, 145.398 (arom) 166.130, 167.144 (C=N)

1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium chloride. To a suspension of AgOTf (1.90 g, 7.4 mmol) in 50 mL CH₂Cl₂ was added chloromethyl
pivalate (1.11g, 7.4mmol) and the resulting suspension was stirred for 45 min. The supernatant was transferred via syringe to vial containing a solution of 1,4-bis(2,4,6-trimethylphenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene (2.26g, 5.1mmol) in CH₂Cl₂, and the resulting solution was stirred in a sealed tube in the dark at 40 °C for 20 h. After the solution was cooled to room temperature, the reaction was quenched with methanol and the solvent evaporated in vacuo. The resulting oil was chromatographed on silica gel (CH₂Cl₂/MeOH) to give 1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium trifluoromethanesulfonate as a yellow oil. The oil was then dissolved in 50 mL CH₂Cl₂, 10 g IRA-900 resin was added and the suspension was stirred overnight. After filtration, the solvent was pumped off under vacuum. The product was washed with pentane at room temperature to give a yellow solid (1.9g, 78% yield). ¹H NMR (CDCl₃, 23 °C, 400 MHz): δ 2.183 (s, 12 H, ortho-CH₃), 2.325 (s, 6 H, para-CH₃), 6.983 (s, 4H, meta-CH on IMes), 7.026 (d, 4H, ortho-CH on Ph ), 7.308 (m, 6H, meta-, para-CH on Ph ), 10.518 (s, 1H, im-²H) ¹³C NMR (CDCl₃, 23 °C, 100 MHz): δ 18.414 (ortho-CH₃), 21.586 (para-CH₃), 125.355, 129.376, 129.444, 130.034, 130.308, 130.568, 132.525, 134.869, 141.619 (arom C) ) MS FAB {(CH₃)₃C₆H₂(C₆H₅)₂C₃N₂H}⁺ m/e 457.2 (M+, 100), 458.3 (M +1, 30) HRMS: Cald for C₃₃H₃₃N₂H M⁺, 457.2644; found: 457.2633.

1,3-dimethylimidazol-4,5-diphenyl-2-ylidene (1). KO'Bu (0.1g, 0.89mmol) and 1,3-(2,4,6-trimethylphenyl)-4,5-diphenyl-imidazolium chloride (0.44g, 0.89mmol) were added to 20 mL THF. The solution was stirred for 30 min then filtered, and all volatiles were removed under vacuum. The products were washed with pentane at room temperature to leave a yellow solid (0.30g, 75% yield). ¹H NMR (CDCl₃, 23 °C, 400 MHz): δ 2.177 (s, 12 H, ortho-CH₃), 2.347 (s, 6 H, para-CH₃), 6.823 (s, 4H, meta-CH on IMes), 6.983 (m, 6H, meta-, para-CH on Ph ), 7.206 (d, 4H, ortho-CH on Ph ), ¹³C NMR (CDCl₃, 23 °C, 100 MHz): δ 18.369 (ortho-CH₃), 21.579 (para-CH₃), 125.359, 129.367, 129.417, 130.033, 130.301, 130.555, 132.446, 134.865, 141.611 (arom C), 242.132 (s, im-²C) MS, HRMS: Cald for C₃₃H₃₃N₂ H⁺ M⁺+1, 457.2644; found: 457.2641.

Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 1. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoullian integration percentages for a given $P_i$ (at left in table).

\[ P_i = 0.59 \]
Figure S2. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 4. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given $P_i$ (at left in table).

$$P_i = 0.90$$

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Predicted Bernoulian Integration Percentages for a given $P_i$
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 7. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given $P_i$ (at left in table).

$P_i = 0.62$

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Predicted Bernoulian Integration Percentages for a given $P_i$
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Figure S4. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the PLA methine resonances with selective decoupling of the PLA methyl resonances from the sample made in Table 1, entry 9. The experimental integration values shown were determined by deconvoluting the overlapping peaks using the line fitting procedure of the Nuts software application and then normalizing the total of the five peaks to be one. On the bottom is a table showing various predicted Bernoulian integration percentages for a given $P_i$ (at left in table).

\[
P_i = 0.83
\]
Figure S5. An illustrative line fit of the spectra (Table 1, entry 2). The fits were done using the line fitting procedure of the Nuts software application. The blue line is the actual spectra. The red and green lines are the assigned peak fits. The areas of these peaks were then normalized, with the total of all five peaks set to one in order to obtain the relative integrations.
Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of the PLA methine resonances from the sample made in Table 1, entry 4.

Figure S7. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of the PLA methine resonances from the sample made in Table 1, entry 8.
Figure S8. DSC of PLA made with 1 (Table 1, entry 4). This figure is from the second scan (ramp rate of 10 °C/min).