

Electronic Supplementary Information (ESI) for

**Kinetic Study of Carbene Polymerization of Ethyl
Diazoacetate by Palladium and Rhodium catalysts**

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Experimental Section.

Materials. EDA, [(L-prolinate)Rh^I(2,5-norbornadiene)] (Cat-1) and [(L-prolinate)Rh^I(1,5-cyclooctadiene)] (Cat-2) were prepared according to previous literature.¹⁻³ The solvents were purchased from *Sinopharm Chemical Reagent Co., Ltd* and refluxed with calcium hydride overnight and distilled before used. Bis(1,5-cyclooctadiene)dirhodium dichloride was purchased from *Accela* and di-mu-chlorobis(norbornadiene)dirhodium was purchased from *Alfa Aesar*. Bis(acetonitrile)dichloropalladium (PdCl₂(CH₃CN)₂, Cat-3), and palladium chloride (PdCl₂, Cat-5) were purchased from *Aldrich*. Palladium acetate (Pd(OAc)₂, Cat-4) was purchased from *J&K Scientific Ltd*.

Synthesis of [(L-prolinate)Rh^I(1,5-cyclooctadiene)]: Proline (1 mmol, 125 mg) and NaOH (1 mmol, 43 mg) were dissolved in MeOH (10 mL) and then stirred for one hour at room temperature. The solution was added to a suspension of bis(1,5-cyclooctadiene)dirhodium dichloride (0.5 mmol, 0.2465 g) in MeOH (5 mL). The reaction mixture was stirred for 1 h. The solvent was evaporated and the residue was redissolved in CH₂Cl₂ (10 mL) and centrifuged. The supernatant was removed and the remaining solid was dried in vacuum for 24 h. Recrystallization of the product in MeOH (5 mL) with an excess of Et₂O (30 mL) at -20°C yielded yellow crystals (0.107 g, 0.30 mmol, 33%). ¹H NMR (300 MHz, CDCl₃): δ 4.5-3.5 (s, 4H, CH=CH), 3.90 (m, 1H, COOCH), 3.00 (m, 2H, NHCH₂), 2.59 (m, 2H, CH=CHCH₂), 2.40 (m, 2H, CH=CHCH₂), 2.23 (m, 2H, COOCHCH₂), 2.03 (m, 1H, NH-CH₂CH₂), 1.96 (m, 2H, CH=CH-CH₂), 1.78 (m, 2H, CH=CH-CH₂), 1.65 (m, 1H, NHCH₂CH₂) ppm.

Synthesis of [(L-prolinate)Rh^I(1,5-cyclooctadiene)]: Proline (1 mmol, 125 mg) and NaOH (1 mmol, 43 mg) were dissolved in MeOH (10 mL) and then stirred for one hour at room temperature. The solution was added to a suspension of [di-mu-chlorobis(norbornadiene)dirhodium] (0.5 mmol, 250 mg) in MeOH (5 mL). The reaction mixture was stirred for 1 h. The solvent was evaporated and the residue was redissolved in CH₂Cl₂ (10 mL) and centrifuged. The supernatant was removed and the remaining solid was washed with abundant CH₂Cl₂ (30 mL). The mixture was filtrated, and subsequently the solid was dried in vacuum for 24 h. The product was obtained as a yellow powder (251 mg, 0.76 mmol, 76%). ¹H NMR (300 MHz, CDCl₃): δ 4.04, 3.99 (s, 4H, nbd-CH olefinic), 3.89 (s, 2H, nbd-CH), 3.72 (m, 1H, CHCOO), 2.85-2.72 (m, 2H, CH₂NH), 2.18-2.12 (m, 1H, CH₂CH₂CH), 2.06-1.92 (m, 2H, CH₂CH₂CHCOO), 1.70-1.62 (m, 1H, CH₂CH₂CH), 1.26 (s, 2H, nbd-CH₂) ppm.

Equipment.

FTIR spectra were collected on an is10 (Thermo) with an optical fiber (detection range: 1600-3400 cm⁻¹). ¹H and ¹³C NMR spectra were recorded on a Mercury VX-300 spectrometer (300 MHz) using CDCl₃ as solvent and trimethylsilane as the internal standard.

Carbene polymerization of EDA and real-time FTIR observation.

A solution of catalyst in chloroform was prepared under argon atmosphere and the background was collected. Then, ethyl diazoacetate (EDA) was quickly added to the above solution and began the data collection. Upon addition, gas evolution was visible,

and the data was collected every ten seconds. The mixture was stirred at room temperature until the absorption peak at 2110 cm^{-1} vanished already.

Reference

- (1) Jellema, E.; Budzelaar, P. H. M.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2007**, *129*, 11631.
- (2) Hetterscheid, D. G. H.; Hendriksen, C.; Dzik, W. I.; Smits, J. M. M.; van Eck, E. R. H.; Rowan, A. E.; Busico, V.; Vacatello, M.; Castelli, V. V.; Segre, A.; Jellema, E.; Bloemberg, T. G.; de Bruin, B. *J. Am. Chem. Soc.* **2006**, *128*, 9746.
- (3) Qi, H. Z.; Yang, Z. H.; Xu, J. X. *Synthesis* **2011**, 723.

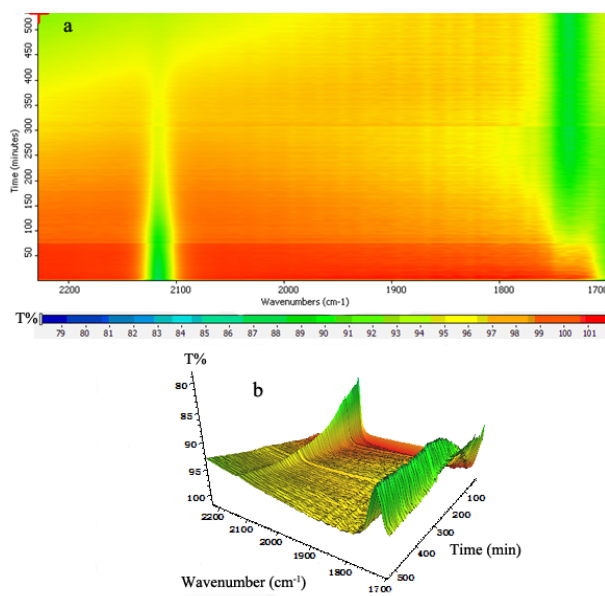


Figure S1. 2D (a) and 3D (b) reaction processes for the Cat-2 catalyzed EDA polymerization.

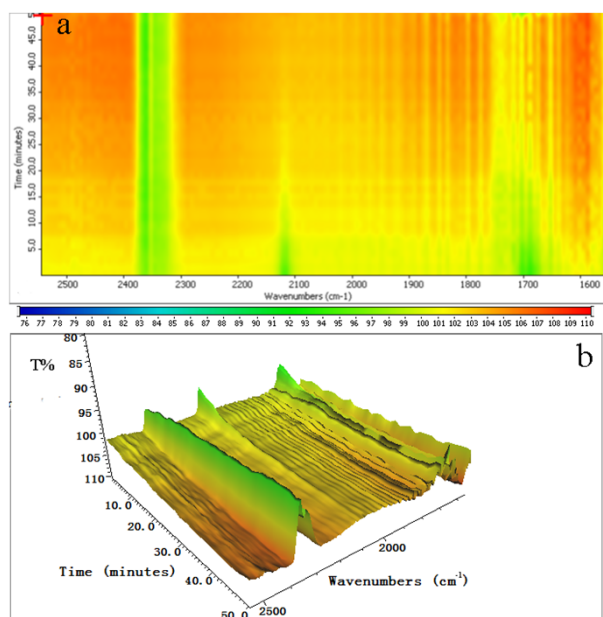


Figure S2. 2D (a) and 3D (b) reaction processes for the Cat-3 catalyzed EDA polymerization.

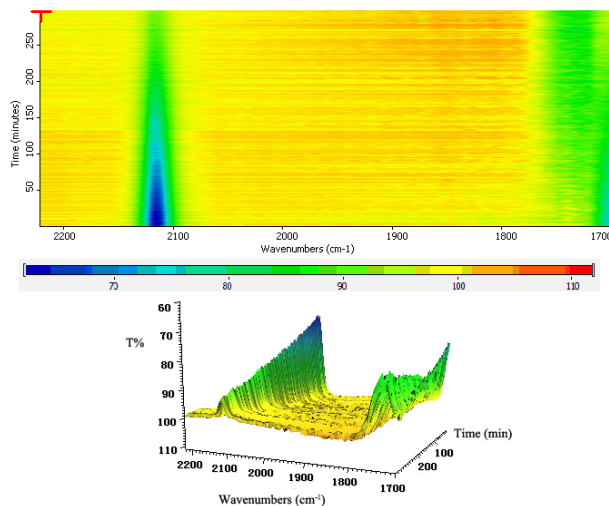


Figure S3. 2D (a) and 3D (b) reaction processes for the Cat-4 catalyzes EDA polymerization.

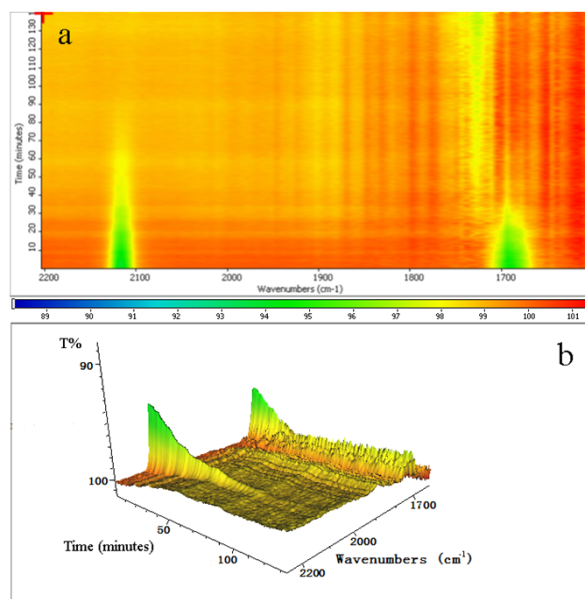


Figure S4. 2D (a) and 3D (b) reaction processes for the Cat-5 catalyzed EDA polymerization.

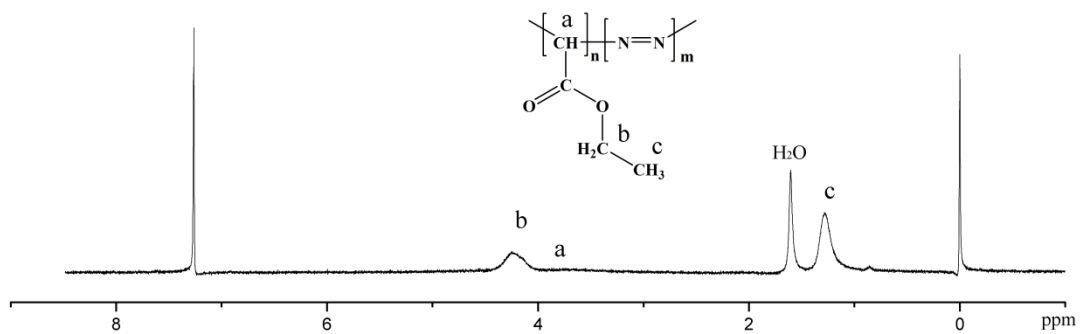


Figure S5. ^1H NMR spectrum of the polymers obtained by Cat-3 mediates EDA polymerization.

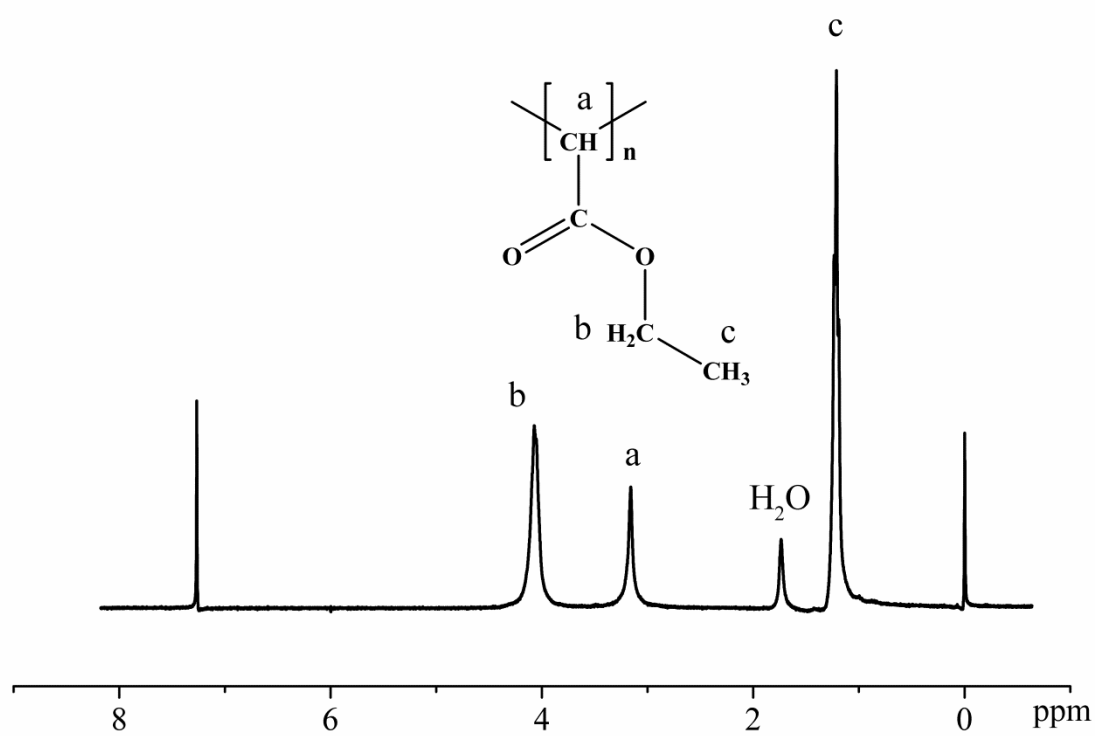


Figure S6. ^1H NMR spectrum of the polymers obtained by Cat-2 mediates EDA polymerization.

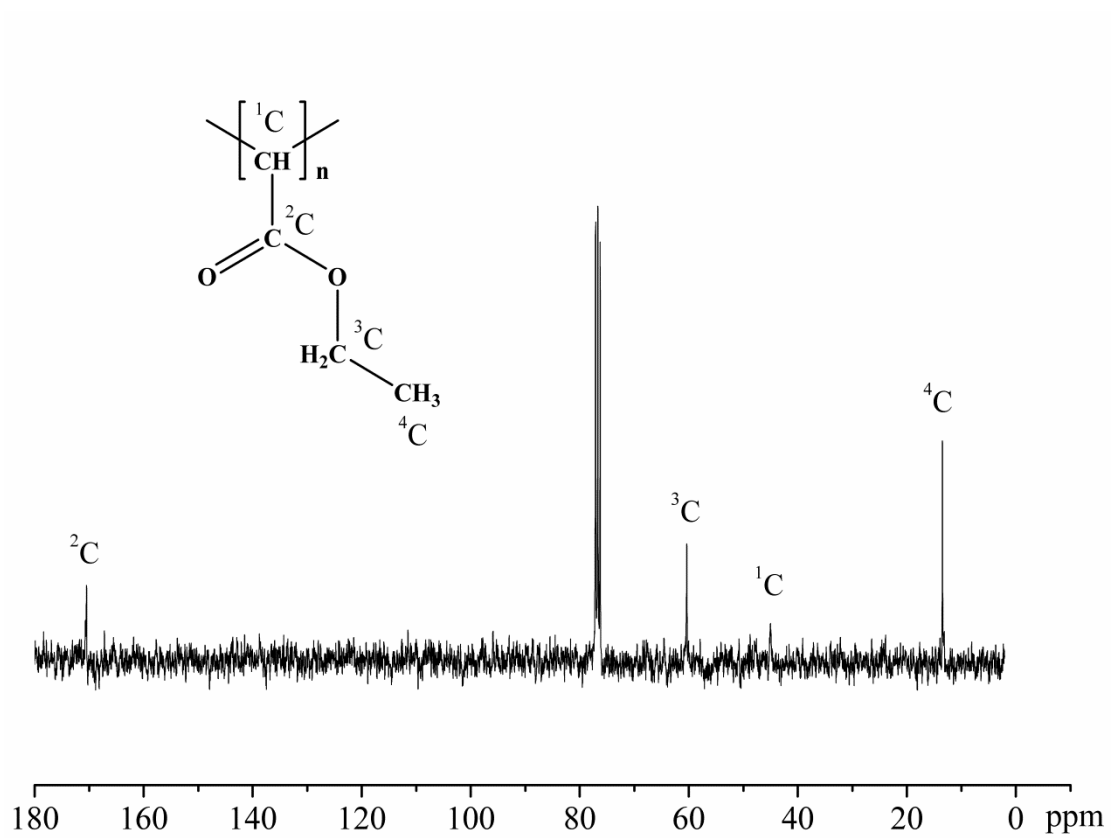


Figure S7. ^{13}C NMR spectrum of the polymers obtained by Cat-2 mediated EDA polymerization.