Supporting Information for

Polymeric Palladium-Mediated Carbene Polymerization

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Table S1. Poly(imidazole-Pd)-mediated polymerization of EDA in the presence of H_2O, CH_3OH and CH_3CH_2OH

| Entry	Additive	Yield (%)	M_n (Da)	PDI
1	None	93	1070	1.08
2	100μL H_2O	77	550	1.16
3	500μL H_2O	53	680	1.17
4	100μL CH_3OH	74	630	1.14
5	500μL CH_3OH	62	480	1.05
6	100μL CH_3CH_2OH	82	620	1.20
7	500μL CH_3CH_2OH	74	890	1.36

Experimental conditions: 30 mg Poly(imidazole-Pd), 0.912 g EDA, 10 ml toluene, 17 h. Crude products were obtained by precipitating from petroleum ether. Yield% = [the weight of the products]/[the weight of monomer-8*10^{-3}*28]*100%. M_n, and PDI (M_w/M_n) were obtained by GPC calibration using standard polystyrenes in THF solution.
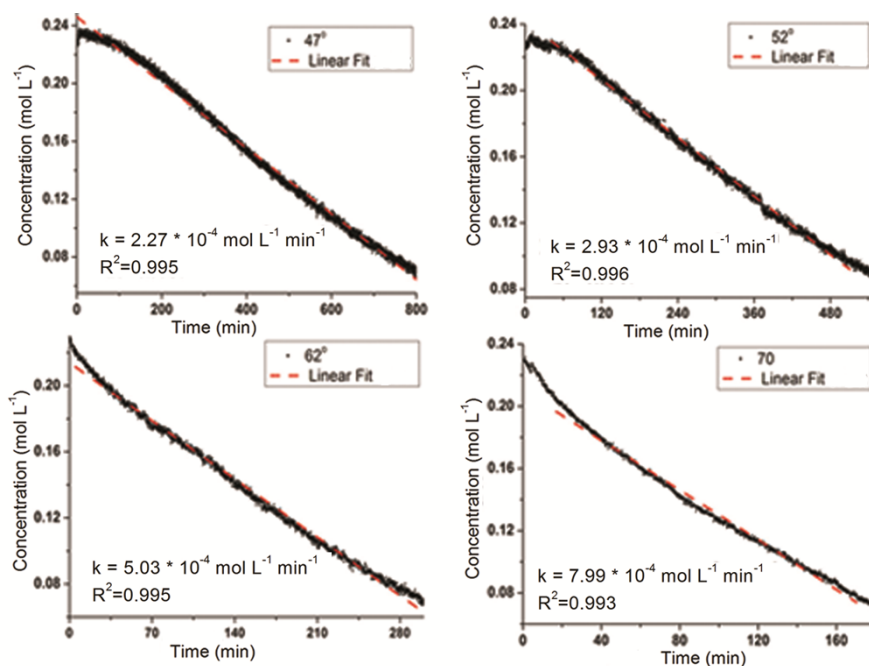
Fig. S1: Zero order kinetics plots fit for poly(imidazole-Pd)-mediated polymerization of EDA at different temperatures (temperatures were set at 47, 52, 62, and 70 ºC).

**Table S2.** Calculation for the apparent activation energy (Ea) value

| T (ºC)	47	52	62	70
1/T	-0.00442	-0.00452	-0.00474	-0.00492
k (mol L^{-1} min^{-1})	0.0002268	0.0002933	0.0005034	0.0007992
$\ln k$	-8.39	-8.13	-7.59	-7.13

$$\ln^k = \ln^A - E_a/RT$$

Ea = 20.9 kJ/mol (Fig. 3d)
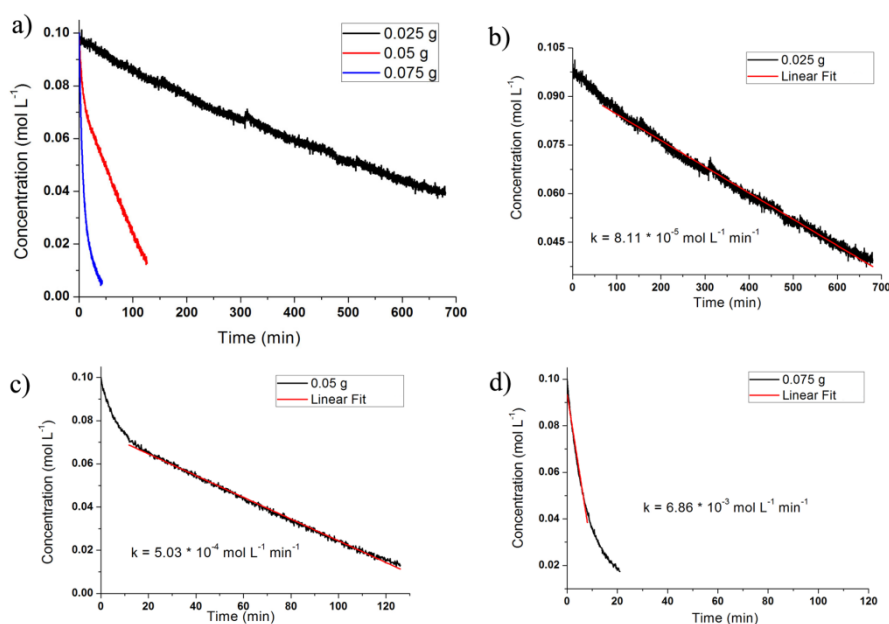
Fig. S2: Zero order kinetics plots for the polymerization reaction mediated by different amount of poly(imidazole-Pd) catalyst (0.025 g, 0.05 g and 0.075 g), 0.1 mol/L EDA, 10 ml toluene, temperatures were set 60 °C.
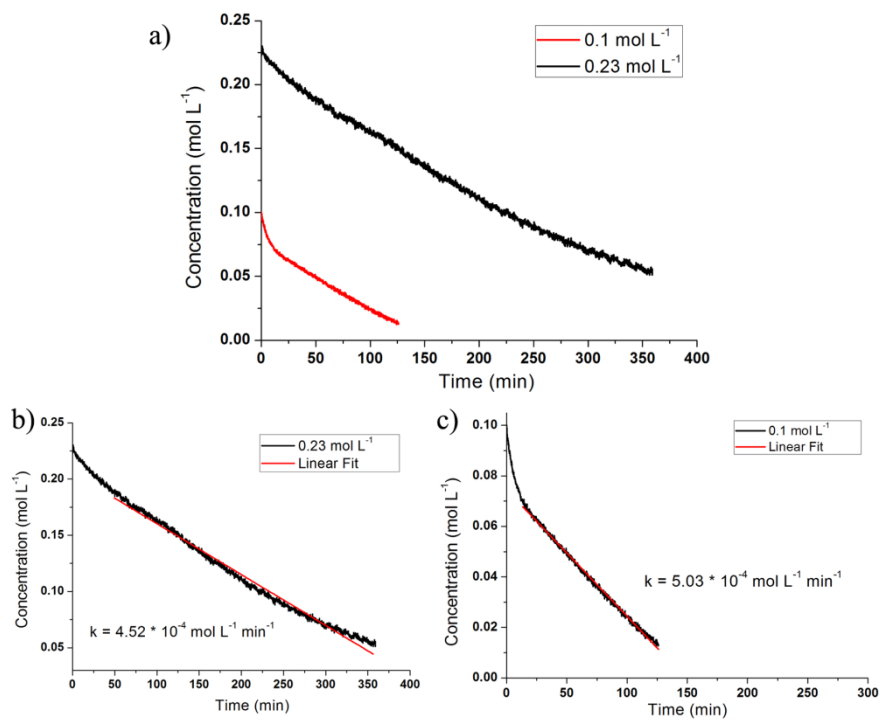
Fig. S3. Zero order kinetics plots for the polymerization reaction with different concentration of EDA (0.1mol/L EDA and 0.23mol/L EDA). 0.05 g poly(imidazole-Pd) catalyst, 10 ml toluene, temperatures were set 60 °C.
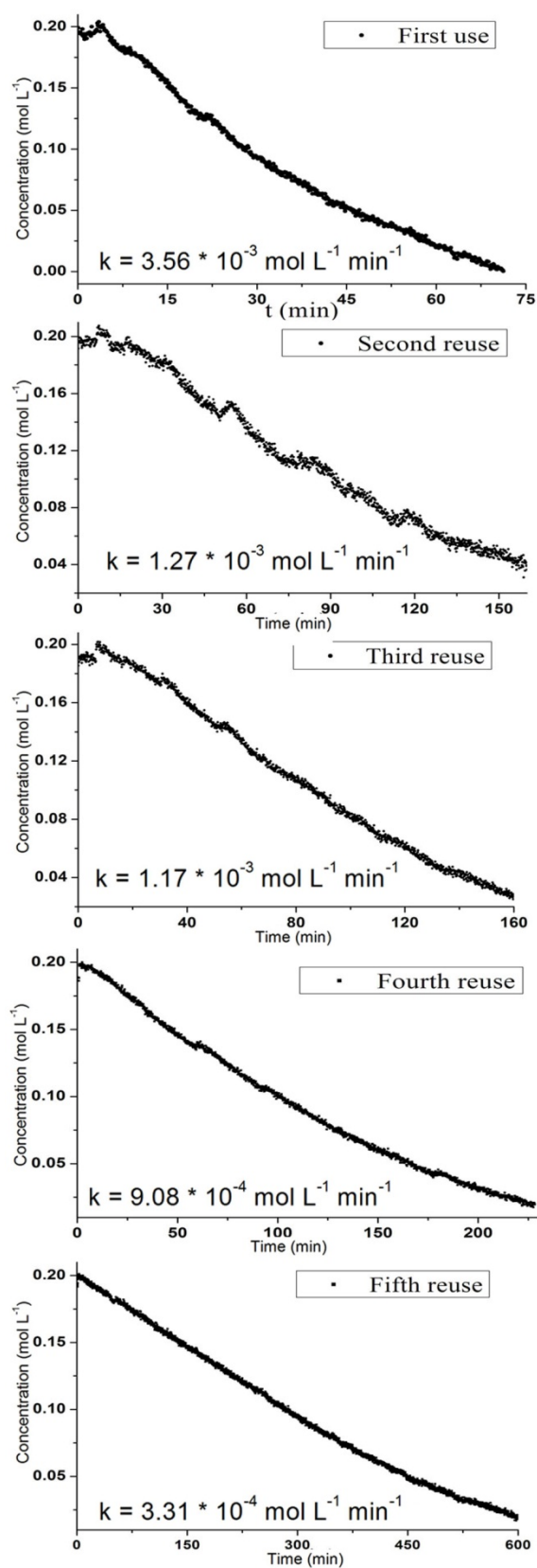
Fig. S4. Zero order plots of the first use, the second reuse, the third reuse, the fourth reuse and the fifth reuse of the poly(imidazole-Pd)- mediated polymerization of EDA (60 ºC, EDA 1 ml, toluene 10 ml).

**Table S3.** Effect of TEMPO on oligomer yields and molecular weight

Entry	[Cat]/[TEMPO]	M_n (Da)	PDI	Yield (%)
1	1:0	1070	1.08	93
2	1:1	670	1.24	38
3	1:3	1000	1.07	33
4	1:10	980	1.05	29
5	1:50	850	1.02	20

Experimental conditions: 30 mg Poly(imidazole-Pd), 0.912 g EDA, 10 ml toluene, 17 h. Crude products were obtained by precipitating from petroleum ether. The [Cat]/[TEMPO] is mass ratio. Yield% = [the weight of the products]/[the weight of monomer-8*10^{-3}*28]*100%. M_n, and PDI (M_w/M_n) were obtained by GPC calibration using standard polystyrenes in THF solution.
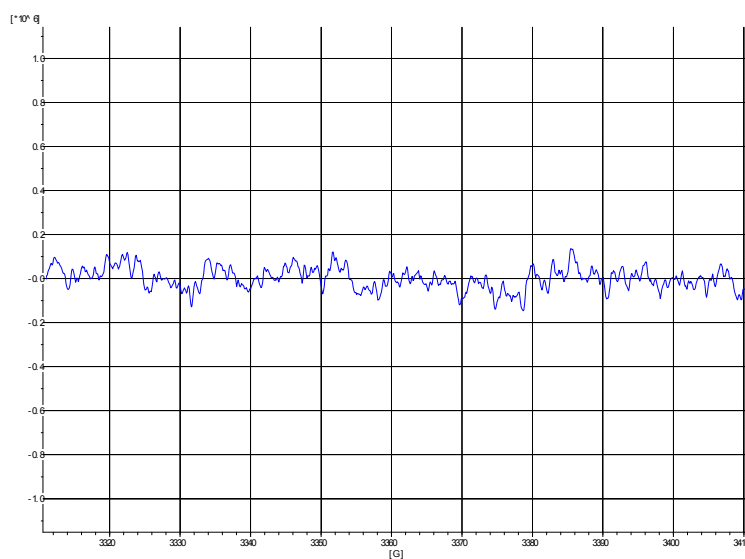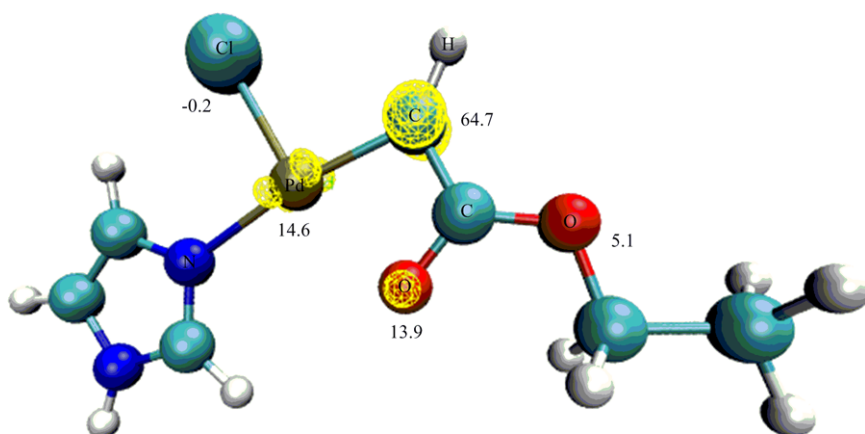

Fig. S5: Spectrum without EPR signals when carbene polymerization reaction was carried out without poly(imidazole-Pd) catalyst.
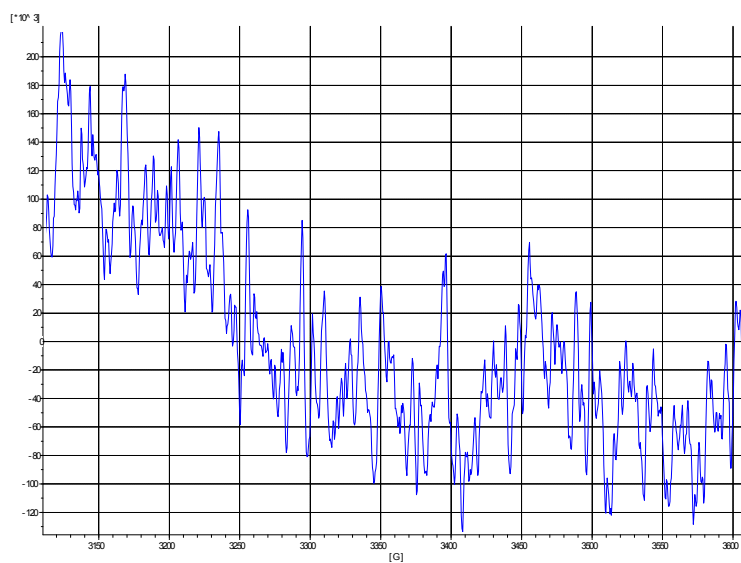
Fig. S6: Spectrum without EPR signals of poly(imidazole-Pd)-mediated polymerization of EDA without PBN.
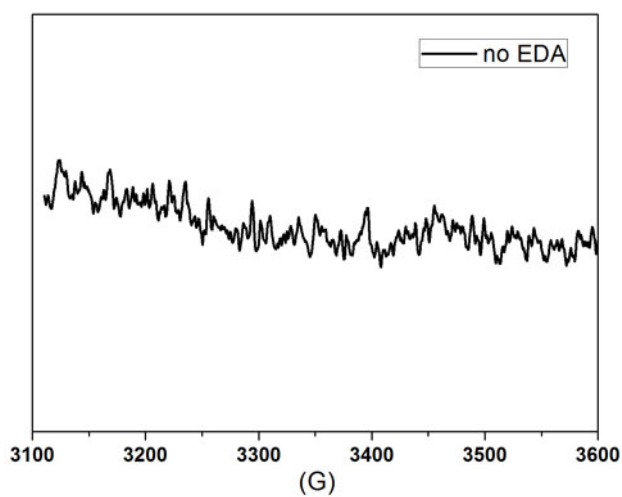

Fig. S7: Spectrum without EPR signals of the PBN and poly(imidazole-Pd) catalyst mixture.

Fig. S8 Calculated molecular structure and Mulliken atom spin density for the Pd-carbene radical

Table S4. Spin distributions of atoms

Atom	Alpha_pop.	Beta_pop.	Spin_pop.	Atomic charge
1(C)	3.36520	2.71806	0.64714	-0.08326
2(H)	0.46284	0.48995	-0.02711	0.04720
3(C)	2.88337	2.84661	0.03675	0.27002
4(O)	4.22152	4.08234	0.13918	-0.30387
5(O)	4.14815	4.09699	0.05116	-0.24514
6(C)	2.94685	2.95001	-0.00316	0.10314
7(H)	0.47786	0.47432	0.00354	0.04781
8(H)	0.47786	0.47432	0.00354	0.04782
9(N)	3.60773	3.61815	-0.01041	-0.22588
10(C)	2.93885	2.92798	0.01087	0.13317
11(C)	2.96819	2.96425	0.00393	0.06756
12(H)	0.46247	0.46313	-0.00066	0.07441
13(C)	2.99419	2.99559	-0.00140	0.01023
14(H)	0.47613	0.47641	-0.00027	0.04746
15(H)	0.42306	0.42327	-0.00021	0.15367
16(H)	0.47926	0.47930	-0.00004	0.04144
17(N)	3.54041	3.53801	0.00240	-0.07843
18(C)	3.03476	3.03478	-0.00002	-0.06954
19(H)	0.47364	0.47347	0.00017	0.05288
20(H)	0.47914	0.47931	-0.00018	0.04155
21(H)	0.47364	0.47347	0.00017	0.05289
22(Cl)	8.63392	8.63629	-0.00237	-0.27020
23(Pd)	9.03095	8.88398	0.14697	0.08507
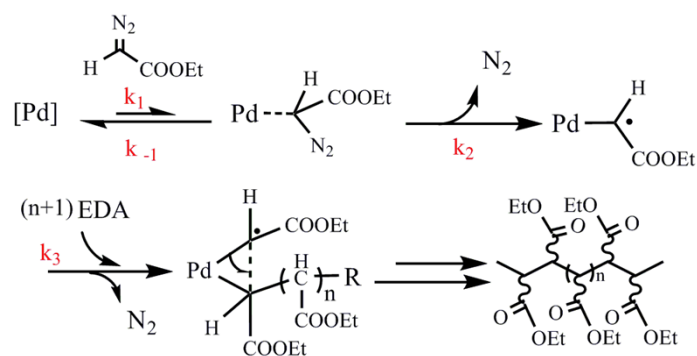
Scheme. S1 Proposed metal-carbene radical polymerization (MCRP) mechanism.

Fig 3C shows the linear fit curve of the zero-order kinetics dependent on EDA. The plot also show the deviation from the kinetic profile at the incipient stage which is designated as the initiation step.

The simulated chemical kinetic equation is expressed as follows: $r_{Pd}=k_{Pd}[Pd]^x[EDA]^y$. Varying the amount of palladium-catalyst and EDA, the processes are consistent with zero-order kinetics (Fig S2 and S3), therefore x=0 and y=0, the rate law is expressed as $r_{Pd}=k_{Pd}$.

The equation indicates that the nitrogen-releasing of EDA is not the rate-limiting step. It should be a fast step. Therefore, it is reasonable to propose that the initiation step (EDA coordinate on the palladium-catalyst to form the Pd-EDA transition state) is the rate limiting step (also the slow step). That means the rate k_1 is much less than k_2 (nitrogen-releasing step) and k_{-1} (the dissociation step) (*RSC Adv.,* 2014, **4**, 41848-41855).

Scheme 3 and Scheme S1 show the pre-equilibrium palladium-EDA binding resulting in a 'saturated' palladium-EDA transition state (the slow initiation step) preceding the fast nitrogen-releasing of EDA step, therefore, add more EDA would not affect the kinetic profile. The rate law derived from the proposed mechanism shows the polymerization process is independent on EDA concentration.