Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplemental Information for

Advanced Chemical Recycling of Poly(ethylene terephthalate) Through Organocatalytic Aminolysis

Kazuki Fukushima,[1,5] Julien M. Lecuyer,[1,2] Di S. Wei,[1,4] Hans W. Horn,[1] Gavin O. Jones,[1] Hamid A. Al-Megren,[3] Abdullah Mohammad,[3] Fares D. Alsewailem,[3] Melanie A. McNeil,[2] Julia E. Rice,[1] and James L. Hedrick[1,*]

[1]*IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120*

[2]*Chemical and Materials Engineering Department, San Jose State University, San Jose, CA 95192*

[3] *King Abdul Aziz City for Science and Technology, Saudi Arabia*

[4] *Physics and Astronomy Department, University of Denver, Denver, CO 80208*

[5] *Yamagata University, Yonezawa, Japan, Department of Biochemical Engineering*

* hedrick@almaden.ibm.com

A. Experimental Investigation of the TBD-Catalyzed Aminolysis of PET

Experimental

Materials

PET beverage bottles were washed with water, dried, and shredded to around 3 mm squares prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), amine reagents, and solvents were purchased from Sigma-Aldrich and used as received.

Measurements

^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 Instrument at 400 MHz. Gas chromatography was carried out with a Agilent Technologies GC system 7890A equipped with a Agilent Technologies HP-5 GC column (30 m × 0.32 mm, 0.25 μm) heated from 80 °C to 240 °C with a ramp rate 15 °C/min under a hydrogen flow of 30 ml/min. Differential scanning calorimetry (DSC) was recorded on a TA Instruments DSC Q2000 with a ramp rate of 5 °C/min under a nitrogen atmosphere. A melting point of the product was determined as the on-set temperature of the melting endotherm. Thermal gravimetric analysis (TGA) was recorded on a TA Instruments TGA Q500 with a ramp rate of 5 °C/min under a nitrogen purge. The absorption spectra were measured by Agilent 8453 UV-Vis spectrometer.

Kinetic study

The aminolysis reaction

$\mathrm{PET} + \mathrm{amine} \rightarrow \mathrm{terephthalamide}$is stoichiometrically rewritten as follows where PET is depicted by an n-mer of ethylene terephthalate (ET)

$$(\mathrm{ET})_n + 2n\ \mathrm{amine} \rightarrow n\ \mathrm{terephthalamide}$$

the rate of PET consumption is given as follows,

$$-\frac{d[\mathrm{PET}]}{dt} = k[\mathrm{PET}][\mathrm{amine}] \quad \text{(Eq. S1)}$$

where k (mol^{-1}s^{-1}) is a rate constant, and [PET] and [amine] are concentrations of ET repeating unit and amine, respectively, at time t.
Integration of Eq. S1 (t = 0 → t) in terms of the stoichiometry gives the following equation,

$$\frac{1}{2[\mathrm{PET}]_0 - [\mathrm{amine}]_0} \ln\left(\frac{[amine]_0[\mathrm{PET}]}{[PET]_0[amine]}\right) = kt \quad \text{(Eq. S2)}$$

where $[PET]_0$ and $[amine]_0$ depict their initial concentration.
The conversion P of PET into a terephthalamide is given by Eq. S3.

$$P = \frac{[PET]_0 - [PET]}{[PET]_0} \quad \text{(Eq. S3)}$$

Eq. S2 can be altered to Eq. S4

$$\frac{1}{2[PET]_0 - [amine]_0} \ln\left(\frac{[amine]_0(1-P)}{[amine]_0 - 2P[PET]_0}\right) = kt \quad \text{(Eq. S4)}$$

$[PET]_0$ = 1.53 M and $[\mathbf{1a}]_0$ = 9.14 M for the reaction involving **1a**, and $[PET]_0$ = 1.76 M and $[\mathbf{1b}]_0$ = 10.9 M for the reaction involving **1b**.

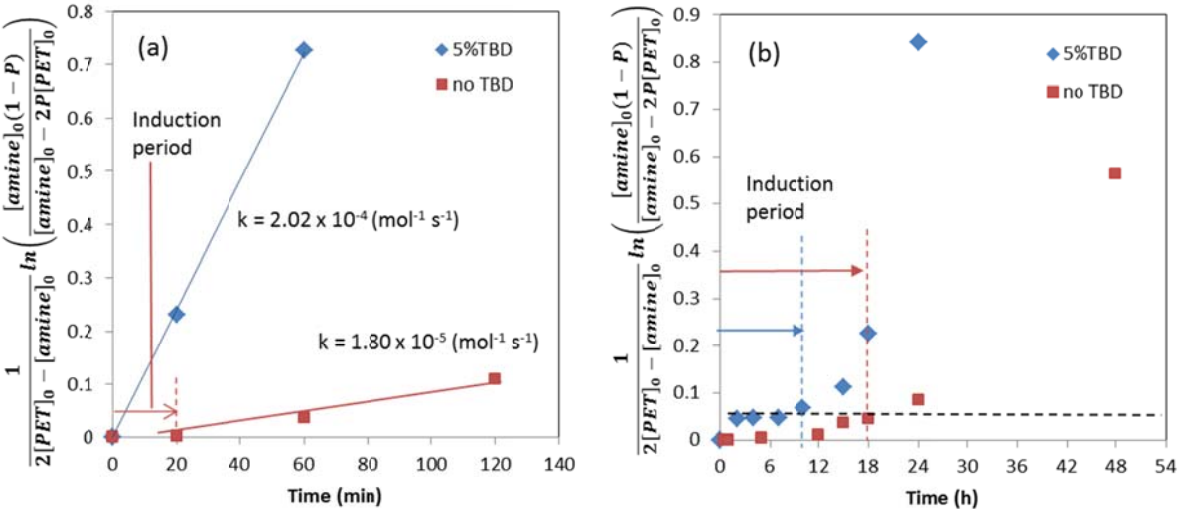


Figure S1. Semilogarithmic plots of time against conversion of PET for the aminolysis to form 2a (a) and 2b (b).

By comparison, when excess amount of amines are used (e.g., 16 eq.), the reaction follows quasi-first-order reaction conditions. Then, Eq. S1 becomes

$$-\frac{d[PET]}{dt} = k[PET] \quad \text{(Eq. S5)}$$

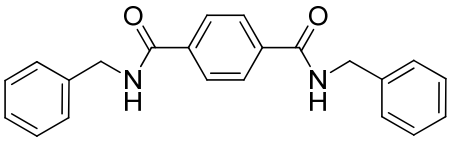
In addition, the Eq. S4 corresponds to

$$\ln\left(\frac{1}{1-P}\right) = kt \quad \text{(Eq. S6)}$$

Most of depolymerizaiton of PET follows a quasi-first order condition and the kinetics is evaluated by Eq. 6.

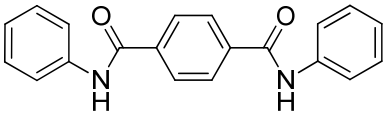
Synthesis of terephthalamide compounds

N,*N*'-dibenzylterephthalamide (**2a**: DBnTA)



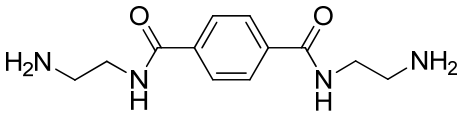
PET flakes (0.48 g, 2.5 mmol), benzylamine (**1a**, 1.60 g, 14.9 mmol) and TBD (17.5 mg, 0.126 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 150 °C for 1 h where the reaction mixture solidified. The mixture was triturated and washed in THF (60 ml). The residue was filtered and dried in a vacuum oven at 80 °C, yielding a white powder as the product (0.75 g, 87%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.18 (t, J = 5.8 Hz, 2H, N*H*), 7.98 (s, 4H, Ar-*H*), 7.37-7.30 (m, 8H, Ar-*H*), 7.28-7.22 (m, 2H, Ar-*H*), 4.50 (d, J = 6.0 Hz, 4H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.5, 139.4, 136.5, 128.2, 127.22, 127.19, 126.7, 42.6. mp (DSC) : 264 °C (lit. 262-264, 264-266 °C [S1]).

N, *N*'-diphenylterephthalamide (**2b**: DPhTA)



PET flakes (0.48 g, 2.5 mmol), aniline (**1b**, 1.45 g, 15.5 mmol) and TBD (17.6 mg, 0.126 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 180 °C for 24 h. The crude product was poured in 60 ml of THF and the insoluble was filtered out. The residue was then dried in vacuum at 50 °C, yielding white powder as the product (0.32 g, 41 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.41 (s, 2H, N*H*), 8.10 (s, 4H, Ar-*H*), 7.80 (d, J = 8.4 Hz, 4H, Ar-*H*), 7.38 (t, J = 7.4 Hz, 4H, Ar-*H*), 7.13 (t, J = 7.4 Hz, 2H, Ar-*H*). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 164.7, 138.9, 137.4, 128.6, 127.7, 123.8, 120.4. mp (DSC) : 265 °C

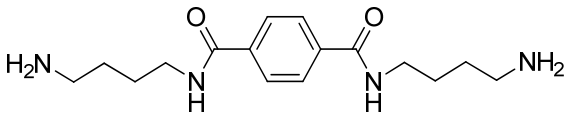
N,*N*'-Bis(2-aminoethyl)terephthalamide (**2c**: BAETA)



PET flakes (0.48 g, 2.5 mmol) were placed into a 25 ml Schlenk tube along with excess amounts of ethylenediamine (**1c**, 2.42 g, 40 mmol) and TBD (17.4 mg, 0.125 mmol). The tube was then heated under nitrogen atmosphere at 110 °C for 1 h. The homogeneous solution was then poured in 50 ml of hot toluene and filtered. The residue was dissolved in methanol (50 ml) to remove a

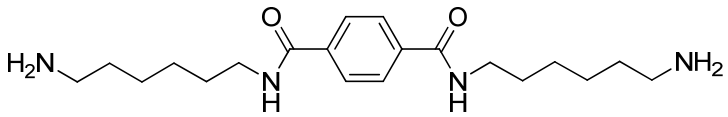
small amount of insoluble by filtration. The filtrate was evaporated under vacuum and the residue was washed with isopropanol and dried in a vacuum oven at 80 °C, yielding a white powder as the product (0.56 g, 89%). ^{1}H-NMR (D_2O containing 0.25% H_2SO_4): δ 7.84 (s, 4H, Ar-*H*), 3.68 (t, *J* = 6.0 Hz, 4H, NH*CH*$_2$), 3.22 (t, *J* = 6.0 Hz, 4H, *CH*$_2$NH$_2$). ^{13}C-NMR (D_2O containing 0.25% H_2SO_4): δ 170.6, 136.3, 127.6, 39.2, 37.3. mp (DSC) : 197 °C.

N,*N*'-Bis(4-aminobutyl)terephthalamide (**2d**: BABTA)



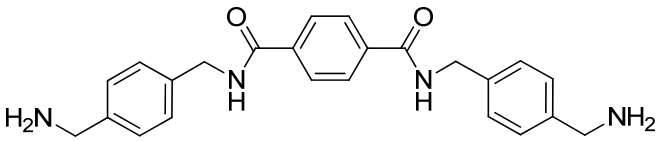
PET flakes (0.48 g, 2.5 mmol), 1,4-diaminobutane (**1d**, 3.56 g, 40 mmol) and TBD (17.4 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 110 °C for 1 h. The homogeneous solution was then poured in 50 ml of hot toluene and filtered. The residue was dissolved in methanol (50 ml) to remove a small amount of insoluble by filtration. The filtrate was evaporated under vacuum and the residue was washed with hot toluene and dried in a vacuum oven at 80 °C, yielding a white powder as the product (0.63 g, 82%). ^{1}H-NMR (D_2O containing 0.25% H_2SO_4): δ 7.78 (s, 4H, Ar-*H*), 3.40 (t, *J* = 6.4 Hz, 4H, NH*CH*$_2$), 3.01 (t, *J* = 7.0 Hz, 4H, *CH*$_2$NH$_2$), 1.77-1.61 (m, 8H, *CH*$_2$). ^{13}C-NMR (D_2O containing 0.25% H_2SO_4): δ 170.0, 136.7, 127.3, 39.2, 39.0, 25.4, 24.2. mp (DSC): 217 °C

N,*N*'-bis(6-aminohexyl)terephthalamide (**2e**: BAHTA)



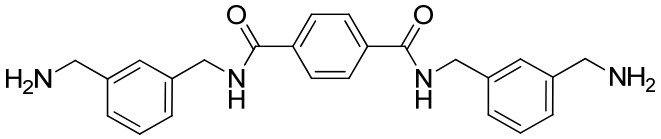
PET flakes (0.48 g, 2.5 mmol), 1,6-diaminohexane (**1e**, 4.66 g, 40 mmol) and TBD (17.3 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 110 °C for 2 h. The homogeneous solution was then poured in 50 ml of hot toluene and filtered. The residue was washed with methanol several times and the filtrates were collected and evaporated under vacuum at 80 °C, yielding a white powder as the product (0.57 g, 63%). ^{1}H-NMR (400 MHz, D_2O containing 0.25% H_2SO_4): δ 7.75 (s, 4H, Ar-*H*), 3.34 (t, *J* = 6.8 Hz, 4H, NH*CH*$_2$), 2.94 (t, *J* = 7.6 Hz, 4H, *CH*$_2$NH$_2$), 1.68-1.53 (m, 8H, *CH*$_2$), 1.37 (quin, *J* = 3.6 Hz, 8H, *CH*$_2$). ^{13}C-NMR (100 MHz, D_2O containing 0.25% H_2SO_4): δ 170.0, 136.8, 127.3, 39.8, 39.3, 28.0, 26.6, 25.5, 25.2. mp (DSC) : 171 °C (lit. 178 °C [S2])

N,*N*'-bis(4-(aminomethyl)benzyl)terephthalamide (**2f**: 4AMBTA)



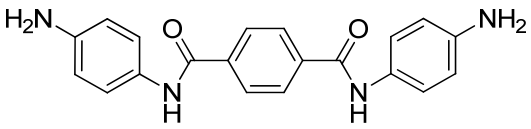
PET flakes (0.48 g, 2.5 mmol), *p*-xylylenediamine (**1f**, 5.45 g, 40 mmol) and TBD (17.4 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 150 °C for 1 h. The homogeneous mixture was cooled down and washed in 50 ml of hot toluene several times to remove unreacted reagent. The residue was finally washed in hot water and dried in a vacuum oven at 80 °C, yielding a white powder as the product (0.80 g, 79%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.14 (t, J = 6.0 Hz, 2H, N*H*), 7.96 (s, 4H, Ar-*H*), 7.26 (q, J = 6.7 Hz, 8H, Ar-*H*), 4.43 (d, J = 6.0 Hz, 4H, NH*CH*$_2$), 3.67 (s, 4H, *CH*$_2$NH$_2$). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.4, 142.8, 137.2, 136.6, 127.2, 127.0, 126.9, 45.3, 42.4. mp (DSC) : 223 °C

N,*N*'-bis(3-(aminomethyl)benzyl)terephthalamide (**2g**: 3AMBTA)



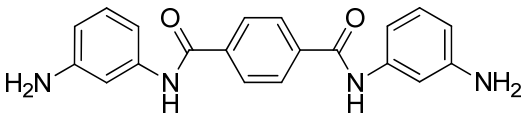
PET flakes (0.48 g, 2.5 mmol), *m*-xylylenediamine (**1g**, 5.48 g, 40 mmol) and TBD (17.3 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 150 °C for 1 h. The homogeneous solution was then poured in 100 ml of water and heated. After insoluble was filtered out, the filtrate was left at 4 °C for 20 h, allowing for precipitation. The precipitate was then dried in a vacuum oven at 80 °C, yielding a white powder as the product (0.68 g, 67%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.16 (t, J = 6.0 Hz, 2H, *NH*), 7.98 (s, 4H, Ar-*H*), 7.31-7.13 (m, 8H, Ar-*H*), 4.48 (d, J = 6.0 Hz, 4H, NH*CH*$_2$), 3.69 (s, 4H, *CH*$_2$NH$_2$). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.4, 144.2, 139.2, 136.5, 128.0, 127.2, 125.9, 125.5, 125.1, 45.5, 42.7. mp (DSC) : 128 °C

N,*N*'-bis(4-aminophenyl)terephthalamide (**2h**: 4APTA)



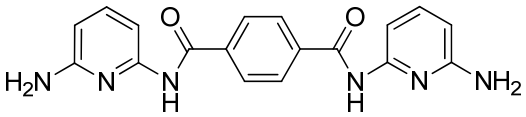
PET flakes (0.48 g, 2.5 mmol), *p*-phenylenediamine (**1h**, 4.09 g, 38 mmol) and TBD (17.7 mg, 0.127 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 190 °C for 18 h. The homogeneous solution was then poured in 100 ml of THF and filtered. The residue was then washed in hot water (50 ml) and dried in a vacuum oven at 80°C, yielding a gray powder as the product (0.63 g, 72%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.0 (s, 2H, *NH*), 8.02 (s, 4H, Ar-*H*), 7.39 (d, J = 8.8 Hz, 4H, Ar-*H*), 6.55 (d, J = 8.8 HZ, 4H, Ar-*H*), 4.97 (s, 4H, *NH*$_2$). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 163.8, 145.3, 137.3, 127.8, 127.3, 122.2, 113.6. mp (DSC) : 301 °C

N,*N*'-bis(3-aminophenyl)terephthalamide (**2i**: 3APTA)



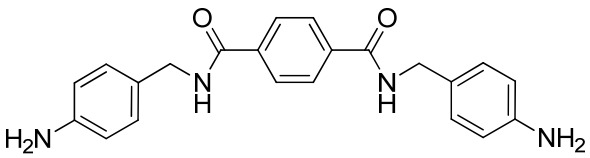
PET flakes (0.48 g, 2.5 mmol), *m*-phenylenediamine (**1i**, 4.40 g, 41 mmol) and TBD (17.6 mg, 0.126 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 190 °C for 18 h. The homogeneous solution was then poured in 100 ml of THF and filtered. The filtrate was concentrated and precipitated in water (100 ml). The residue was then washed in methylene chloride a few times and dried in a vacuum oven at 80 °C, yielding a pale pink powder as the product (0.65 g, 75%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.09 (s, 2H, *NH*), 8.04 (s, 4H, Ar-*H*), 7.12 (s, 2H, Ar-*H*), 6.98 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.33 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.12 (s, 4H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 164.5, 148.9, 139.5, 137.5, 128.8, 127.5, 109.9, 108.3, 106.1. mp (DSC) : 295 °C

N,*N*'-bis(6-aminopyridin-2-yl)terephthalamide (**2j**: 6APYTA)



PET flakes (0.48 g, 2.5 mmol), 2,6-diaminopyridine (**1j**, 4.41 g, 40 mmol) and TBD (17.4 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 190 °C for 18 h. The crude product was poured in 60 ml of THF and the insoluble was filtered out. The filtrate was concentrated and precipitated in water. The residue was then dried in vacuum at 50 °C, yielding reddish brown powder as the product (0.63 g, 72 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 10.31 (s, 2H, N*H*), 8.04 (s, 4H, Ar-*H*), 7.42 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.34 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.26 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 5.82 (s, 4H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 164.8, 158.5, 150.2, 138.8, 137.0, 127.7, 104.1, 102.1. mp (DSC) : 233 °C.

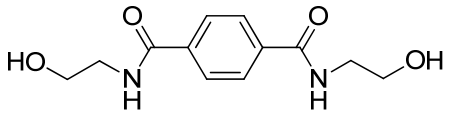
N,*N*'-bis(4-aminobenzyl)terephthalamide (**2k**: 4ABTA)



PET flakes (0.48 g, 2.5 mmol), 4-aminobenzylamine (**1k**, 0.97 g, 7.9 mmol) and TBD (17.2 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 120 °C for 1 h where the reaction mixture solidified. The mixture was triturated and washed in hot toluene (50 ml) and isopropanol (50 ml). The residue was then dried in a vacuum oven at 80 °C, yielding a pale yellowish powder as the product (0.66 g, 70%). ^{1}H-NMR (400 MHz, DMSO-

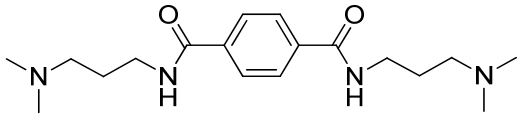
d$_6$): δ 8.96 (t, *J* = 6 Hz, 2H, N*H*), 7.93 (s, 4H, Ar-*H*), 6.98 (d, *J* = 8 Hz, 4H, Ar-*H*), 6.51 (d, *J* = 8 Hz, Ar-*H*), 4.96 (s, 4H, N*H*$_2$), 4.30 (d, *J* = 6 Hz, 4H, C*H*$_2$). ^{13}C-NMR (100 MHz, DMSO-*d*$_6$): δ 165.4, 147.6, 136.7, 128.4, 127.3, 126.4, 113.8, 42.5. m.p. (DSC): 203 °C.

N,*N*'-bis(2-hydroxyethyl)terephthalamide (**2l**: BHETA)



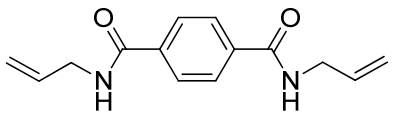
PET flakes (0.48 g, 2.5 mmol), ethanolamine (**1l**, 1.0 g, 16 mmol) and TBD (17.8 mg, 0.128 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 120 °C for 2 h. The slurry was then poured in 50 ml of methylene chloride and filtered. The residue was then washed in 50 ml of THF, filtered, and dried in a vacuum oven at 50 °C, yielding a white powder as the product (0.58 g, 93%). ^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ 8.56 (t, *J* = 5.6 Hz, 2H, N*H*), 7.92 (s, 4H, Ar-*H*), 4.76 (t, *J* = 5.6 Hz, 2H, O*H*), 3.52 (q, *J* = 6.1 Hz, 4H, C*H*$_2$OH), 3.34 (q, *J* = 6.0 Hz, 4H, NHC*H*$_2$). ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 165.6, 136.6, 127.1, 59.6, 42.2. mp (DSC) : 228 °C. (lit. 225-227, 226-228 °C [S3])

N,*N*'-bis(3-(dimethylamino)propyl)terephthalamide (**2m**: DMPTA)



PET flakes (0.48 g, 2.5 mmol), 3-(dimethylamino)-1-propylamine (**1m**, 0.8 g, 7.8 mmol) and TBD (17.4 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 120 °C for 3 h. The slurry was then poured in 50 ml of THF and filtered. The resulting white powder was then dried in a vacuum oven at 50 °C, yielding the product (0.62 g, 74%). ^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ 8.62 (t, *J* = 5.6 Hz, 2H, N*H*), 7.89 (s, 4H, Ar-*H*), 3.28 (q, *J* = 6.5 Hz, 4H, NHC*H*$_2$), 2.25 (t, *J* = 7.0 Hz, 4H, C*H*$_2$N(CH$_3$)$_2$), 2.12 (s, 12H, C*H*$_3$), 1.65 (quin, *J* = 7.2 Hz, 4H, C*H*$_2$). ^{13}C-NMR (400 MHz, DMSO-*d*$_6$): δ 165.3, 136.6, 127.0, 56.9, 45.1, 37.7, 27.0. mp (DSC) : 173 °C.

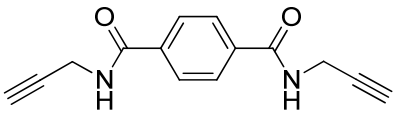
N,*N*'-diallylterephthalamide (**2n**: DATA)



PET flakes (0.48 g, 2.5 mmol), allylamine (**1n**, 0.91 g, 16 mmol) and TBD (17.6 mg, 0.126 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 45 °C for 4 h. The slurry was then washed in 50 ml of ethyl acetate and filtered. The resulting white

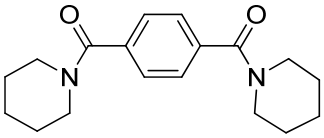
powder was then dried in a vacuum oven at 50 °C, yielding the product (0.50 g, 81%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.79 (t, J = 5.6 Hz, 2H, N*H*), 7.93 (s, 4H, Ar-*H*), 5.95-5.84 (m, 2H, C*H*), 5.21-5.06 (m, 4H, CHC$H_2$5), 3.91 (t, J = 5.6 Hz, 4H, CH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.3, 136.5, 135.2, 127.1, 115.2.41.5. mp (DSC) : 220 °C. (lit. 215, 221 °C [S4])

N,*N*'-di(prop-2-yn-1-yl)terephthalamide (**2o**: DPTA)



PET flakes (0.48 g, 2.5 mmol), propargylamine (**1o**, 3.05 g, 55 mmol) and TBD (17.2 mg, 0.124 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 70 °C for 135 h. The homogeneous solution was then poured in 250 ml of ethyl acetate and filtered. The resulting orange sticky substance was then dried in a vacuum oven at 50 °C, yielding a white powder as the product (0.40 g, 66%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.08 (t, J = 5.4 Hz, 2H, *NH*), 7.93 (s, 4H, Ar-*H*), 4.07 (q, J = 2.5 Hz, 4H, CH_2), 3.15 (t, J = 2.4 Hz, 2H, *CH*). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.2, 136.2, 127.3, 81.1, 73.0, 28.5. mp (DSC) : 205 °C.

1,4-phenylenebis(piperidin-1-ylmethanone) (**2p**: PBPD)



PET flakes (0.48 g, 2.5 mmol), piperidine (**1p**, 1.30 g, 15 mmol) and TBD (17.4 mg, 0.125 mmol) were placed in a 25 ml Schlenk tube and then heated under nitrogen atmosphere at 100 °C for 16 h. The homogeneous solution was then poured in 50 ml of water and filtered. The resulting white powder was then dried in a vacuum oven at 50 °C, yielding a white powder as the product (0.54 g, 72%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.41 (s, 4H, Ar-*H*), 3.58 (b, 4H, NCH_aH$_b$), 3.26 (b, 4H, NCH$_a$$H_b$), 1.67-1.37 (m, 12H, C$H_2$). ^{13}C-NMR (400 MHz, DMSO-d_6): δ 168.1, 137.2, 126.6, 47.8, 42.2, 25.9, 25.2, 23.9. mp (DSC) : 208 °C (lit. 203-205 °C[S5])

B. Computational Investigation on the Self-Catalyzed Aminolysis of Methylformate

The reactant/catalyst ammonia dimer in Schaefer's study [S6] on the ammonolysis of methylformate (MF) bears a striking resemblance to EDA (Fig. S1a-b), thus we modeled the aminolysis of MF with EDA (Fig. S1c).

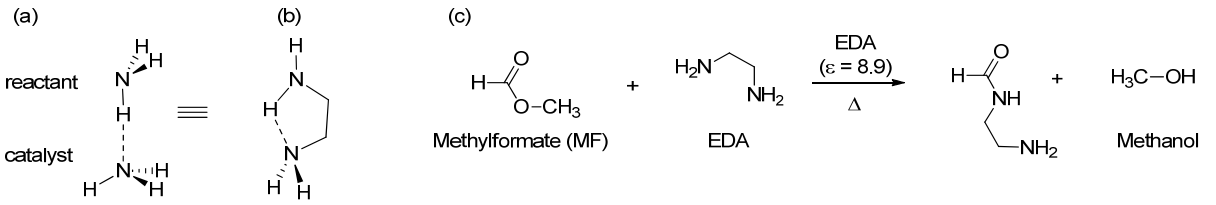


Figure S2. Comparison of models of (a) two ammonia molecules during self-catalysis (*N*-*N* distance = 3.2 Å) and (b) an EDA molecule (*N*-*N* distance = 3.0 Å). (c) Reaction scheme for the aminolysis of methylformate (MF) by excess EDA.

The rate determining barrier for this model system is 30.3 kcal/mol (Fig. S2), which is significantly higher than the corresponding barrier of 24.7 kcal/mol [S6] involving two ammonia molecules under otherwise identical conditions. This is probably because the geometry of the transition state (TS1 in Fig. S3) forms a highly strained 5-membered ring during the proton transfer between the "reactant" and "catalyst" amine group (see Fig. S1b). Subsequently we allowed the "catalyst" amine group to reside on another EDA molecule by modeling the reaction using two EDA molecules (middle of Fig. S3), lowering the barrier by about 8 kcal/mol (22.4 kcal/mol). Finally we modeled the reaction using three EDA molecules (bottom of Fig. S3) with the third EDA acting as a co-catalyst stabilizing any build-up of negative charge at the carbonyl-oxygen in a manner analogous to the role EG plays during the glycolysis of PET [S7]; this lowers the barrier by another 2 kcal/mol (20.4 kcal/mol). While there are certainly entropic arguments against mechanisms involving steps with as many compounds as this (ester + 3 EDA), the experimental conditions are such that the reaction occurs in the condensed phase with EDA being present in high excess, making this a possibility.

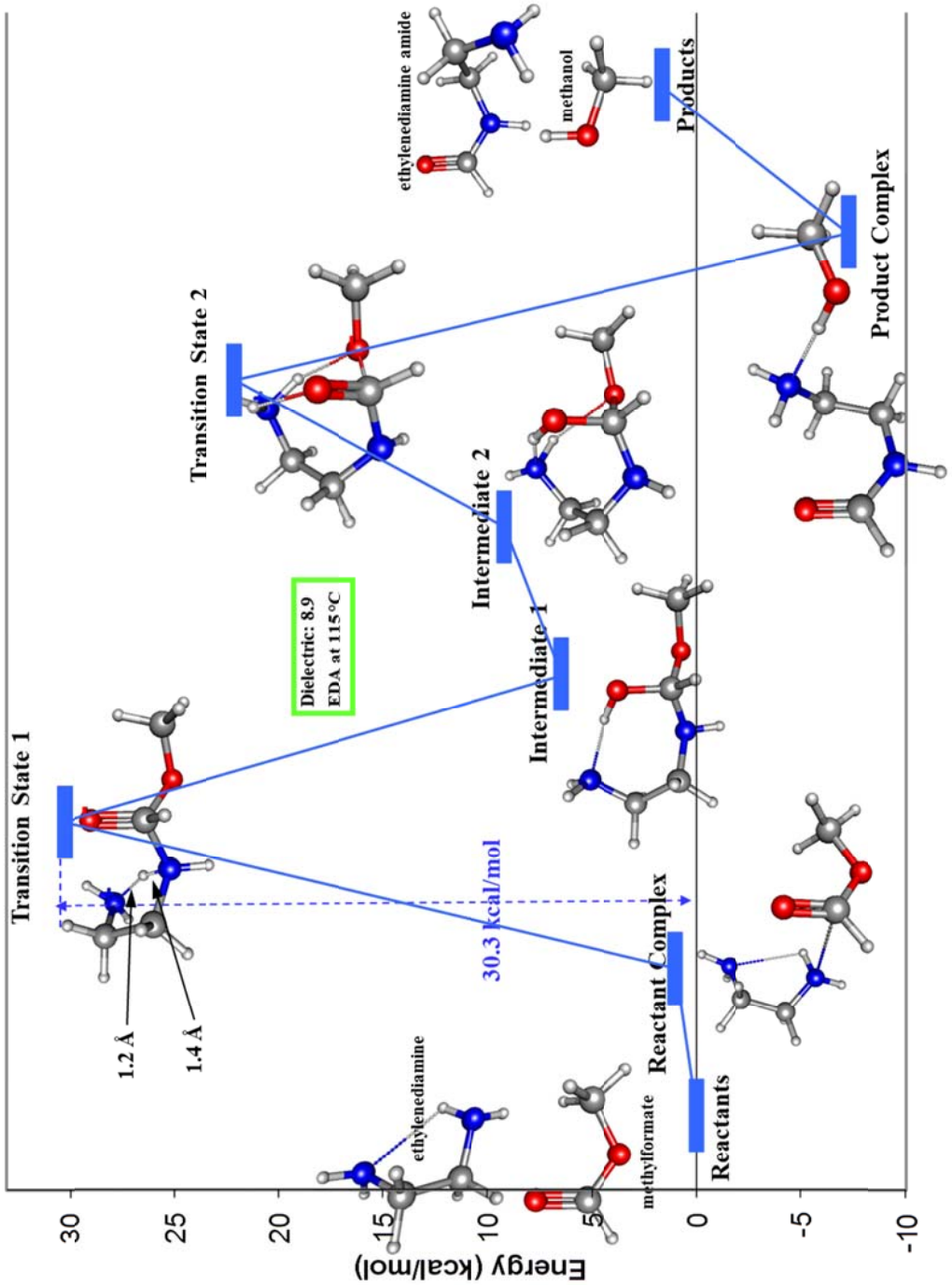


Figure S3. Complete reaction pathway for aminolysis of methylformate with 1 EDA molecule (in continuum EDA)

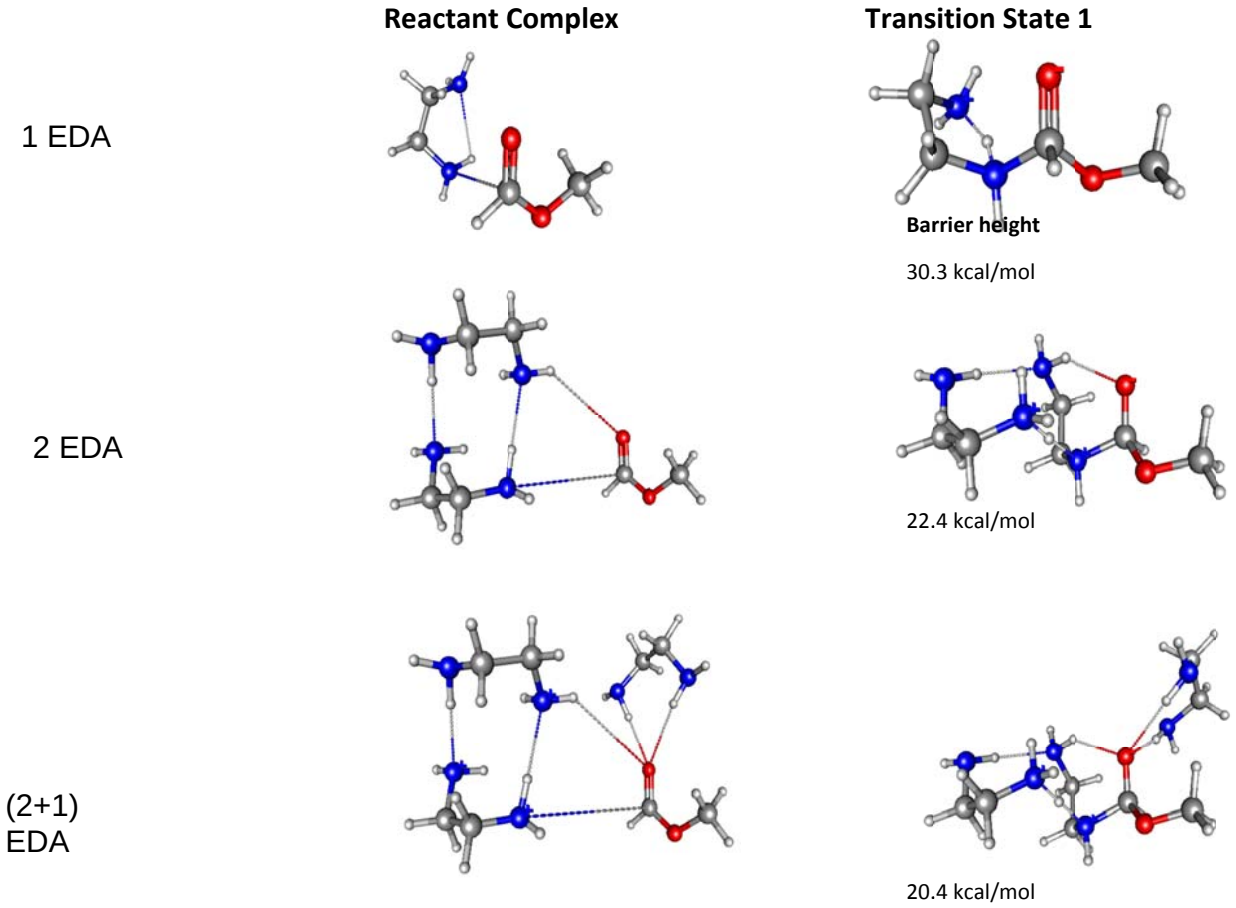


Figure S4. Comparison of the rate limiting step geometries (Transition State 1) in 1 EDA, 2 EDA, and (2+1) EDA pathways for the aminolysis of methylformate with EDA.

C. Cartesian Coordinates for Optimized Geometries of Ground States and Transition States: Aminolysis of MF and DMT in EDA with EDA

GAMESS/US grid settings:

```
$dft    nrad=96 nleb=590 $end ! error in #Elec(grid) < 10-4
$tescav ntsall=240 $end
```

Gradient tolerance [a.u.]: 0.0002 for minima, 0.000075 for saddle points

```
$pcm solvnt=INPUT rsolv=2.40 eps=8.9 $end ! INPUT=EDA @115°C
```

Reactants

```
12
EDA # E(6-31+G*)=-190.53526947; E(ACCPVTZ//6-31+G*)=-190.61226608 H
   C          -0.70270         -0.54751          0.15788
   C           0.78452         -0.47941         -0.18116
   N           1.46258          0.52474          0.65367
   N          -1.36487          0.73346         -0.15389
   H          -0.81619         -0.72848          1.23308
   H          -1.14993         -1.40354         -0.37341
   H           0.89276         -0.28242         -1.26324
   H           1.23850         -1.45873          0.01306
   H           0.99948          1.42294          0.51662
   H           2.42654          0.64381          0.34546
   H          -2.31401          0.73646          0.21641
   H          -1.45668          0.83869         -1.16448

8
MF # E(6-31+G*)=-229.08242767; E(ACCPVTZ//6-31+G*)=-229.16683543 H
   C          -0.00011         -1.32468          0.00003
   O           0.75953         -0.22732          0.00015
   O          -1.21522         -1.34609          0.00011
   C           0.06791          1.04733          0.00008
   H           0.63639         -2.21868         -0.00027
   H           0.85498          1.79991         -0.00012
   H          -0.55170          1.13467         -0.89506
   H          -0.55178          1.13486          0.89508

6
MeOH # E(6-31+G*)=-115.73206389; E(ACCPVTZ//6-31+G*)=-115.78216212 H
   O           1.08132          0.19610          0.00002
   C          -0.34963          0.12517          0.00000
   H           1.43696         -0.70655         -0.00003
   H          -0.72801         -0.38520          0.89511
   H          -0.72817         -0.38515         -0.89505
   H          -0.71246          1.15563         -0.00005

24
DMT # E(6-31+G*)=-688.04557318; E(ACCPVTZ//6-31+G*)=-688.27890647 H
   C          -1.32925          0.43147          0.00006
   C          -1.04550         -0.93204          0.00014
   C           0.28797         -1.37150          0.00005
   C           1.32925         -0.43147         -0.00006
   C           1.04550          0.93204         -0.00014
   C          -0.28797          1.37150         -0.00005
   C          -0.64476          2.82242         -0.00012
   O          -1.79183          3.24476         -0.00012
   O           0.43380          3.62292         -0.00010
   C           0.18421          5.04663          0.00021
   H          -2.35757          0.77738          0.00016
   H          -1.85505         -1.65298          0.00027
   H           2.35757         -0.77738         -0.00016
   H           1.85505          1.65298         -0.00027
   H           1.17081          5.50867          0.00007
   H          -0.37484          5.32940          0.89514
   H          -0.37531          5.32991         -0.89427
   C           0.64476         -2.82242          0.00012
   O           1.79183         -3.24476          0.00012
   O          -0.43380         -3.62292          0.00010
   C          -0.18421         -5.04663         -0.00021
   H          -1.17080         -5.50867         -0.00007
   H           0.37531         -5.32991          0.89427
```

```
   H          0.37484        -5.32940        -0.89514
```

Aminolysis of MF in EDA with 1 EDA

```
20
MF_EDA_RC # E(6-31+G*)=-419.61584114; E(ACCPVTZ//6-31+G*)=-419.77751825 H
   C          0.93186        -0.61996         2.72769
   O          1.45493         0.60243         2.84062
   O         -0.24647        -0.90012         2.82683
   C          0.52826         1.69127         3.07748
   H          1.72882        -1.34984         2.53727
   H          1.14955         2.58148         3.16519
   H         -0.15984         1.78238         2.23434
   H         -0.02940         1.51526         3.99976
   C         -1.14289        -0.97496        -1.74468
   C          0.31946        -0.93347        -2.18296
   N          1.07481         0.04500        -1.38560
   N         -1.80690         0.31178        -2.03012
   H         -1.18602        -1.13971        -0.66193
   H         -1.63665        -1.83042        -2.23357
   H          0.35676        -0.72838        -3.26852
   H          0.76274        -1.92528        -2.02968
   H          0.58876         0.94043        -1.42760
   H          1.99650         0.19511        -1.79367
   H         -2.73736         0.32526        -1.61496
   H         -1.94690         0.41174        -3.03590

20
MF_EDA_TS1 # E(6-31+G*)=-419.57424796; E(ACCPVTZ//6-31+G*)=-419.73081476 H
   C          1.73875         0.67603         1.38347
   C          1.18600        -0.75330         1.07694
   N         -0.18647        -0.57038         0.57629
   N          0.53333         1.51493         1.63547
   H          2.24708         1.07619         0.50849
   H          2.41166         0.68399         2.24208
   H          1.15077        -1.35500         1.98912
   H          1.82660        -1.25813         0.34821
   H         -0.24965         0.70670         1.13739
   H         -0.82945        -1.27417         0.93565
   H          0.54415         2.39949         1.13114
   H          0.35177         1.69333         2.62281
   C         -0.29154        -0.45923        -0.94000
   O         -1.76126        -0.36743        -1.07594
   O          0.39567         0.53271        -1.41719
   C         -2.16818        -0.42988        -2.43429
   H         -0.03258        -1.46659        -1.35339
   H         -3.26102        -0.38171        -2.44986
   H         -1.75825         0.40719        -3.01344
   H         -1.84737        -1.37473        -2.90296

20
MF_EDA_INT1 # E(6-31+G*)=-419.60835196; E(ACCPVTZ//6-31+G*)=-419.76880049 H
   N          2.08250        -1.06901        -0.64093
   H          1.94759        -1.82339        -1.31371
   H          3.06497        -0.80806        -0.69627
   C          1.73618        -1.52683         0.72163
   H          2.29501        -0.91317         1.43520
   H          2.01996        -2.57655         0.88775
   C         -0.89569         0.53626        -0.13989
   H         -1.88238         0.05460        -0.27559
   O         -1.12230         1.91318         0.11758
   O         -0.18318         0.32081        -1.32286
```

```
   N          -0.16696          0.05680          1.01362
   C          -2.04083          2.52061         -0.79052
   H          -2.15721          3.55739         -0.46750
   H          -3.01851          2.01852         -0.75764
   H          -1.65680          2.49856         -1.81703
   C           0.23844         -1.35854          1.01125
   H           0.75498          0.03770         -1.10415
   H          -0.69948          0.28621          1.84770
   H           0.03566         -1.78086          2.00171
   H          -0.35195         -1.94423          0.28964

20
MF_EDA_INT2 # E(6-31+G*)=-419.60419362; E(ACCPVTZ//6-31+G*)=-419.76449348 H
   N           0.25621         -1.71855         -0.66436
   H           0.30846         -2.63709         -1.09935
   H           0.61106         -1.04725         -1.34405
   C           1.07734         -1.67357          0.56988
   H           2.09558         -1.31627          0.36532
   H           1.15631         -2.69284          0.96367
   C          -0.56610          1.07400          0.33181
   H          -1.01977          2.01819          0.65728
   O           0.19017          1.31530         -0.85570
   O          -1.63366          0.19565          0.07077
   N           0.36937          0.62518          1.34593
   C          -0.55736          1.94719         -1.89600
   H           0.15632          2.19189         -2.68610
   H          -1.02571          2.87350         -1.53199
   H          -1.33520          1.28607         -2.29453
   C           0.43924         -0.81165          1.66202
   H          -1.22344         -0.64981         -0.26333
   H           0.19299          1.14280          2.20174
   H           1.05940         -0.89426          2.56155
   H          -0.55120         -1.22848          1.90546

20
MF_EDA_TS2 # E(6-31+G*)=-419.58811571; E(ACCPVTZ//6-31+G*)=-419.74391074 H
   N           0.16259         -1.47195         -0.62150
   H           0.35033         -2.19932         -1.31436
   H           0.34507         -0.50435         -1.01031
   C           0.95895         -1.63856          0.64094
   H           1.98979         -1.35719          0.40904
   H           0.93568         -2.69447          0.92412
   C          -0.75780          1.05077          0.48708
   H          -0.98816          2.12499          0.62591
   O           0.18001          1.18268         -0.84969
   O          -1.75771          0.24871          0.29394
   N           0.19971          0.65025          1.50784
   C          -0.52022          1.80055         -1.91638
   H           0.17528          1.94488         -2.75126
   H          -0.90714          2.78656         -1.61207
   H          -1.36771          1.18897         -2.25848
   C           0.36411         -0.77458          1.76679
   H          -0.84797         -1.40669         -0.39763
   H           1.08544          1.13872          1.39888
   H           1.01608         -0.89106          2.63978
   H          -0.61634         -1.17893          2.03736

20
MF_EDA_PC # E(6-31+G*)=-419.62869263; E(ACCPVTZ//6-31+G*)=-419.79068670 H
   N           0.31395         -0.82256         -0.77767
   H           0.92100         -1.56389         -1.12729
   H           1.36553          0.64846         -0.43158
   C          -0.48746         -1.33901          0.34661
```

```
   H          0.19583        -1.83153         1.04731
   H         -1.22618        -2.08450         0.02625
   C         -2.78348         0.39738        -0.75469
   H         -3.60419         1.11650        -0.91455
   O          1.94425         1.44294        -0.26433
   O         -2.44675        -0.39223        -1.64606
   N         -2.24896         0.51851         0.47545
   C          3.28248         0.99497        -0.07524
   H          3.36819         0.30715         0.77922
   H          3.90204         1.87417         0.12729
   H          3.67728         0.49183        -0.97071
   C         -1.16774        -0.22880         1.14426
   H         -0.32840        -0.59613        -1.53952
   H         -2.67192         1.24125         1.04791
   H         -0.41018         0.49946         1.45653
   H         -1.59531        -0.67399         2.05081

14
MF_EDA_product # E(6-31+G*)=-303.89220575; E(ACCPVTZ//6-31+G*)=-304.00590181 H
   N         -0.44599        -1.63333         1.22514
   H         -1.41427        -1.48133         1.50683
   C         -0.25428        -1.28681        -0.18747
   H          0.79851        -1.45848        -0.43749
   H         -0.84757        -1.98195        -0.79427
   C          1.31754         1.65524        -0.37334
   H          1.74662         2.43718         0.27480
   O          1.88297         1.28546        -1.40736
   N          0.14047         1.17843         0.08231
   C         -0.64131         0.14564        -0.59850
   H          0.13079        -1.04159         1.82162
   H         -0.21978         1.58032         0.93912
   H         -0.49647         0.26909        -1.67653
   H         -1.69723         0.33214        -0.37487
```

Aminolysis of MF in EDA with 2 EDA

```
32
MF_2EDA_RC # E(6-31+G*)=-610.15574035; E(ACCPVTZ//6-31+G*)=-610.39312559 H
   C         -0.36069        -3.81107         3.39707
   O         -0.52829        -4.87219         2.60581
   O         -1.23442        -3.04242         3.74823
   C         -1.87166        -5.12170         2.11957
   H          0.69312        -3.72694         3.69146
   H         -1.79000        -6.01393         1.50061
   H         -2.21768        -4.27072         1.52896
   H         -2.54657        -5.29406         2.96073
   C         -1.40728         2.65610        -1.53778
   C         -2.16049         1.84384        -0.48566
   N         -1.23825         1.00737         0.30732
   N         -0.42097         3.55993        -0.92095
   H         -0.94873         1.96153        -2.26220
   H         -2.13703         3.26431        -2.08590
   H         -2.74750         2.53275         0.14364
   H         -2.86593         1.17532        -0.99402
   H         -0.69842         1.60905         0.92976
   H         -1.77417         0.39212         0.91857
   H          0.44107         3.05067        -0.69298
   H         -0.14959         4.27612        -1.59311
   C          2.03016         0.38029        -1.95708
   C          3.00676         1.16840        -1.08626
   N          2.29270         1.97630        -0.07787
   N          1.21585        -0.54812        -1.15321
```

```
   H          1.41368         1.09098        -2.53345
   H          2.61153        -0.20605        -2.67901
   H          3.72417         0.46704        -0.62952
   H          3.57476         1.85566        -1.72499
   H          1.91386         1.35471         0.63696
   H          2.95473         2.58033         0.40824
   H          0.43049        -0.04858        -0.71929
   H          0.79481        -1.24705        -1.76364

32
MF_2EDA_TS1 # E(6-31+G*)=-610.12653708; E(ACCPVTZ//6-31+G*)=-610.35746400 H
   H         -0.63240        -0.25752         0.07138
   C         -2.23205         2.05853        -0.43910
   C         -2.65357         0.79632         0.31294
   N         -1.46600         0.09148         0.87421
   N         -1.42113         2.93408         0.41823
   H         -1.71426         1.77450        -1.36973
   H         -3.14661         2.58505        -0.73197
   H         -3.32828         1.05394         1.13556
   H         -3.16717         0.10078        -0.35747
   H         -0.99226         0.69141         1.55337
   H         -1.74200        -0.75648         1.37292
   H         -0.43268         2.65292         0.36719
   H         -1.47275         3.89409         0.08301
   C          1.12789         0.19644        -1.59215
   C          2.10206         1.05777        -0.78426
   N          1.46723         1.64630         0.40783
   H          0.38935         0.84109        -2.08399
   H          1.69623        -0.31462        -2.38317
   H          2.98343         0.45646        -0.51997
   H          2.44249         1.86465        -1.44419
   H          1.42355         0.88052         1.09161
   H          2.08948         2.35243         0.80158
   H         -0.13822        -1.39610        -1.45293
   C          1.18953        -1.71478         0.10044
   H          2.02899        -2.11835        -0.51863
   O          0.23234        -2.84505         0.21278
   O          1.54372        -1.16567         1.22678
   C          0.76659        -3.92114         0.96580
   H          1.00025        -3.61407         1.99258
   H          0.01030        -4.71174         0.98528
   H          1.68316        -4.31779         0.49853
   N          0.36284        -0.79544        -0.79447
```

Aminolysis of MF in EDA with 2+1 EDA

```
44
MF_3EDA_RC # E(6-31+G*)=-800.67739609; E(ACCPVTZ//6-31+G*)=-801.00557566 H
   N          3.99418         0.37564         0.87623
   C          4.62697         1.58971         1.42437
   C          3.59098         2.62156         1.86377
   N          2.87739         2.19725         3.08279
   H          3.51156        -0.14672         1.60802
   H          5.29708         1.37920         2.27508
   H          5.23603         2.03121         0.62634
   H          4.11247         3.55754         2.09865
   H          2.91470         2.82311         1.01594
   H          2.31600         1.36446         2.90367
   H          2.22064         2.92401         3.36491
   H          4.71199        -0.24973         0.51242
   C          1.34608        -1.93154         3.41774
```

```
   O          1.85097        -0.93510         2.93539
   H          1.51551        -2.95077         3.04905
   O          0.51558        -1.95357         4.45846
   C          0.19330        -0.67687         5.06806
   H         -0.48938        -0.91437         5.88234
   H         -0.28817        -0.02574         4.33559
   H          1.10249        -0.20667         5.44832
   C         -2.44431         1.67747        -2.97255
   C         -1.46066         2.03540        -1.85990
   N         -0.87854         0.82463        -1.24904
   N         -1.78785         0.92081        -4.05264
   H         -3.29669         1.13249        -2.53226
   H         -2.83658         2.61100        -3.39407
   H         -0.69027         2.70983        -2.26855
   H         -1.99850         2.58146        -1.07533
   H         -0.22426         0.40233        -1.90813
   H         -0.31858         1.08570        -0.43837
   H         -1.70575        -0.07059        -3.79711
   H         -2.37296         0.94318        -4.88670
   C         -3.46835        -2.17390        -1.86131
   C         -2.60069        -2.98015        -2.82649
   N         -1.42108        -2.20569        -3.25828
   N         -2.71752        -1.78804        -0.65334
   H         -3.88241        -1.30241        -2.39601
   H         -4.31450        -2.80201        -1.55728
   H         -2.32311        -3.93237        -2.34521
   H         -3.19180        -3.21877        -3.71904
   H         -0.77617        -2.12046        -2.47231
   H         -0.91312        -2.72390        -3.97452
   H         -2.16176        -0.94374        -0.83522
   H         -3.37092        -1.53488         0.08651

44
MF_3EDA_TS1 # E(6-31+G*)=-800.66581508; E(ACCPVTZ//6-31+G*)=-800.97299099 H
   N         -3.47716        -0.82403         1.50503
   C         -3.30990        -0.88311         2.96851
   C         -2.34086        -1.98981         3.37968
   N         -0.94135        -1.61447         3.10749
   H         -2.57341        -0.69280         1.03694
   H         -2.95328         0.06701         3.40391
   H         -4.29162        -1.09443         3.41173
   H         -2.44139        -2.16121         4.45929
   H         -2.64665        -2.92061         2.87077
   H         -0.81211        -1.36946         2.11722
   H         -0.33194        -2.40951         3.29665
   H         -4.05371        -0.01968         1.25997
   C          0.05795        -1.33880        -0.52698
   O         -0.68151        -0.57481         0.23500
   H          0.43480        -2.26886        -0.03510
   H          0.73856         0.57580        -1.65864
   C          2.28625         2.85474        -2.45309
   C          1.00278         2.34497        -3.10816
   N          0.18959         1.55522        -2.14028
   N          1.98603         3.62307        -1.23720
   H          2.96430         2.00567        -2.26690
   H          2.78603         3.50723        -3.17695
   H          0.40191         3.18671        -3.46715
   H          1.23654         1.69402        -3.95598
   H         -0.09315         2.14993        -1.35800
   H         -0.66975         1.21439        -2.57523
   H          1.87691         2.98477        -0.43795
   H          2.76378         4.24204        -1.01637
   C          2.43016        -0.44478        -0.21839
```

```
   C          2.11930         0.21502         1.12785
   N          1.31918         1.44237         0.97239
   H          3.15828         0.16510        -0.76635
   H          2.89807        -1.42123        -0.02597
   H          1.62286        -0.51069         1.78671
   H          3.08064         0.47048         1.58941
   H          0.35817         1.11573         0.81516
   H          1.31085         1.94718         1.85887
   H          1.57125        -1.16749        -1.92016
   O         -0.57834        -1.79872        -1.77677
   C         -1.69593        -2.64059        -1.52921
   H         -2.46214        -2.12486        -0.93886
   H         -2.10872        -2.92360        -2.50204
   H         -1.39130        -3.55361        -0.99224
   N          1.26003        -0.61428        -1.11863
```

Aminolysis of DMT in EDA with 1 EDA

```
36
DMT_1EDA_RC # E(6-31+G*)=-878.57863860; E(ACCPVTZ//6-31+G*)=-878.88906003 H
   C          0.03398        -1.19281         1.42948
   C          0.89176        -2.17058         0.93193
   C          2.21964        -1.84296         0.61439
   C          2.67508        -0.52935         0.80206
   C          1.81685         0.44786         1.29973
   C          0.48871         0.12096         1.61522
   C         -0.47274         1.13266         2.14923
   O         -1.62992         0.88174         2.45159
   O          0.07236         2.35360         2.27349
   C         -0.79005         3.40053         2.77076
   H         -0.99404        -1.43789         1.67471
   H          0.53373        -3.18402         0.79029
   H          3.70242        -0.28314         0.55489
   H          2.17350         1.46217         1.43833
   H         -0.16688         4.29376         2.79908
   H         -1.15021         3.14855         3.77087
   H         -1.63645         3.54213         2.09489
   C          3.17974        -2.85356         0.07805
   O          4.34167        -2.60707        -0.21112
   O          2.63249        -4.07323        -0.05480
   C          3.49330        -5.11768        -0.56172
   H          2.87142        -6.01176        -0.58756
   H          4.34568        -5.25870         0.10687
   H          3.84441        -4.86173        -1.56404
   C         -3.34138         1.14858        -1.92495
   C         -2.00400         1.27167        -2.65158
   N         -1.11733         2.21188        -1.95170
   N         -4.05547         2.43977        -1.93033
   H         -3.15520         0.87388        -0.88060
   H         -3.92340         0.33423        -2.38684
   H         -2.19732         1.55793        -3.70200
   H         -1.52185         0.28646        -2.67278
   H         -1.59919         3.10589        -1.86315
   H         -0.27946         2.38416        -2.50518
   H         -4.87661         2.38848        -1.32932
   H         -4.40525         2.63759        -2.86819

36
DMT_1EDA_TS1 # E(6-31+G*)=-878.52701764; E(ACCPVTZ//6-31+G*)=-878.83305272 H
   C         -0.55037        -4.04877         0.27124
   C         -0.99125        -2.60492         0.67905
   N          0.11989        -2.03212         1.45552
```

N	0.47477	-4.44538	1.27650
H	-0.07328	-4.03429	-0.70651
H	-1.38772	-4.74801	0.26542
H	-1.87974	-2.64085	1.31534
H	-1.22408	-2.01664	-0.21188
H	0.64988	-3.30144	1.69015
H	-0.19798	-1.52038	2.27591
H	1.31759	-4.83911	0.86240
H	0.12404	-5.07957	1.99381
C	1.15913	-1.23627	0.64238
O	1.66802	-1.95578	-0.30439
C	0.49475	0.09868	0.19081
O	2.07529	-0.90548	1.76877
C	3.28608	-0.29160	1.35233
H	3.80715	-0.90839	0.61046
H	3.91165	-0.18794	2.24408
H	3.11075	0.70742	0.92484
C	-0.58111	2.22537	0.68603
C	0.04326	1.05657	1.11426
C	0.31320	0.35192	-1.17350
C	-0.30926	1.52105	-1.61471
C	-0.76695	2.46865	-0.68557
C	-1.44599	3.72546	-1.09823
O	-1.88282	4.56449	-0.32027
O	-1.53986	3.85858	-2.43628
C	-2.18975	5.05164	-2.92334
H	-0.92743	2.96022	1.40635
H	0.19366	0.89272	2.17787
H	0.67233	-0.38483	-1.88469
H	-0.44237	1.69724	-2.67700
H	-2.15981	4.97044	-4.00966
H	-3.22262	5.09110	-2.56880
H	-1.64907	5.94022	-2.58868

Aminolysis of DMT in EDA with 2 EDA

48
DMT_2EDA_RC # E(6-31+G*)=-1069.11920972; E(ACCPVTZ//6-31+G*)=-1069.50508841 H

C	1.01117	-3.81642	2.36432
C	0.88560	-3.94450	0.98353
C	-0.24705	-3.43210	0.33112
C	-1.24713	-2.78969	1.07626
C	-1.12145	-2.66155	2.45729
C	0.01066	-3.17523	3.10968
C	0.19321	-3.06520	4.58846
O	1.16991	-3.48805	5.18969
O	-0.83412	-2.44882	5.19554
C	-0.74217	-2.29720	6.63006
H	1.88359	-4.21048	2.87471
H	1.66177	-4.44129	0.41278
H	-2.11888	-2.39304	0.56678
H	-1.89739	-2.16369	3.02764
H	-1.66195	-1.79233	6.92308
H	0.13002	-1.69183	6.88753
H	-0.66956	-3.27702	7.10749
C	-0.42833	-3.55096	-1.14709
O	-1.41820	-3.16148	-1.74938
O	0.61808	-4.13739	-1.75042
C	0.53603	-4.30484	-3.18350
H	1.46721	-4.79473	-3.46568
H	0.44831	-3.33160	-3.67193
H	-0.32250	-4.92976	-3.43986

C	-0.67278	4.37316	-3.53348
C	-1.30571	3.03561	-3.91286
N	-1.12206	2.03388	-2.84444
N	-1.27812	4.93073	-2.31152
H	0.41817	4.23719	-3.44017
H	-0.84433	5.07792	-4.35623
H	-2.36862	3.19983	-4.15454
H	-0.81376	2.65593	-4.81656
H	-1.72695	2.27259	-2.05833
H	-1.44336	1.12266	-3.16955
H	-0.86853	4.49364	-1.47728
H	-1.05299	5.92225	-2.24277
C	2.10362	3.12005	-0.72612
C	1.37278	3.47743	0.56720
N	-0.08795	3.52083	0.36068
N	1.68433	1.80345	-1.23759
H	1.94424	3.92719	-1.46112
H	3.17847	3.08240	-0.51133
H	1.66356	2.75872	1.35087
H	1.69588	4.47379	0.89267
H	-0.43112	2.56916	0.22874
H	-0.54474	3.86243	1.20572
H	0.81281	1.89118	-1.77374
H	2.38034	1.45717	-1.89635

48
DMT_2EDA_TS1 # E(6-31+G*)=-1069.07199385; E(ACCPVTZ//6-31+G*)=-1069.45940808 H

C	-1.04785	0.04627	-0.11123
O	-1.60514	0.73745	0.83124
C	-0.36073	-1.27514	0.33582
H	-0.82445	1.96775	-1.35702
C	0.13408	4.38104	-2.57448
C	-1.18503	3.66856	-2.87265
N	-1.61120	2.83913	-1.71131
N	0.03431	5.17303	-1.34056
H	0.95083	3.64120	-2.54307
H	0.34355	5.05084	-3.41533
H	-1.96909	4.40105	-3.09079
H	-1.07711	3.00407	-3.73519
H	-1.78323	3.43851	-0.90151
H	-2.48400	2.34438	-1.90460
H	0.20440	4.57082	-0.52456
H	0.75551	5.89190	-1.33027
C	1.25934	1.24099	-0.34072
C	1.18172	1.93763	1.02043
N	0.20704	3.04317	1.02749
H	1.75092	1.90629	-1.06097
H	1.89015	0.34772	-0.23754
H	0.96071	1.19526	1.79833
H	2.17978	2.34193	1.22799
H	-0.71085	2.59068	1.10385
H	0.33189	3.59079	1.87912
H	0.14275	0.36090	-1.80490
O	-1.95879	-0.31017	-1.25156
C	-3.17645	-0.90938	-0.83747
H	-3.70405	-0.27472	-0.11571
H	-3.79125	-1.03129	-1.73470
H	-3.00995	-1.89949	-0.38610
N	-0.04918	0.88082	-0.94618
C	0.74209	-3.38684	-0.16566
C	0.11441	-2.21824	-0.59062
C	-0.19370	-1.54064	1.69983
C	0.43169	-2.70896	2.13765

```
   C          0.90850        -3.64423         1.20539
   C          1.58364        -4.90434         1.61489
   O          2.02841        -5.73699         0.83470
   O          1.66291        -5.04838         2.95263
   C          2.30567        -6.24636         3.43727
   H          1.10393        -4.11128        -0.88886
   H         -0.02191        -2.04552        -1.65453
   H         -0.56796        -0.81480         2.41433
   H          0.55019        -2.89560         3.19986
   H          2.26680        -6.17217         4.52380
   H          3.34134        -6.28637         3.09112
   H          1.76535        -7.13124         3.09234
```

Aminolysis of DMT in EDA with 2+1 EDA

```
60
DMT_3EDA_RC # E(6-31+G*)=-1259.65497743; E(ACCPVTZ//6-31+G*)=-1260.11748926 H
   C          1.91628        -3.32077         3.00342
   C          1.79078        -3.44902         1.62271
   C          0.65727        -2.93791         0.97064
   C         -0.34217        -2.29530         1.71613
   C         -0.21681        -2.16656         3.09698
   C          0.91528        -2.68057         3.74896
   C          1.09804        -2.57022         5.22798
   O          2.07502        -2.99295         5.82856
   O          0.07089        -1.95378         5.83488
   C          0.16290        -1.80227         7.26953
   H          2.78829        -3.71556         3.51392
   H          2.56649        -3.94650         1.05199
   H         -1.21284        -1.89597         1.20754
   H         -0.99267        -1.66847         3.66719
   H         -0.75690        -1.29748         7.56262
   H          1.03503        -1.19681         7.52670
   H          0.23578        -2.78216         7.74684
   C          0.47743        -3.05691        -0.50696
   O         -0.51384        -2.66689        -1.11010
   N         -3.56346        -1.48975        -1.00132
   C         -4.42537        -1.99812        -2.08485
   C         -3.79459        -1.78136        -3.45758
   N         -2.63179        -2.66316        -3.66984
   H         -2.71508        -2.05127        -0.92156
   H         -4.66827        -3.06833        -1.97376
   H         -5.36821        -1.43966        -2.04481
   H         -4.53893        -2.02918        -4.22390
   H         -3.55024        -0.71120        -3.56647
   H         -1.87312        -2.42595        -3.03025
   H         -2.26230        -2.52155        -4.60916
   H         -4.04880        -1.58161        -0.10988
   O          1.52196        -3.64062        -1.11129
   C          1.44093        -3.80988        -2.54473
   H          2.37252        -4.29982        -2.82564
   H          1.35433        -2.83669        -3.03289
   H          0.58304        -4.43563        -2.80040
   C          0.23228         4.86823        -2.89406
   C         -0.40067         3.53065        -3.27333
   N         -0.21670         2.52923        -2.20476
   N         -0.37304         5.42580        -1.67213
   H          1.32322         4.73209        -2.80069
   H          0.06075         5.57291        -3.71686
   H         -1.46362         3.69477        -3.51495
   H          0.09120         3.15093        -4.17709
```

```
   H          -0.82222          2.76743         -1.41901
   H          -0.53801          1.61822         -2.52997
   H           0.03632          4.98858         -0.83784
   H          -0.14784          6.41730         -1.60336
   C           3.00853          3.61504         -0.08670
   C           2.27769          3.97258          1.20658
   N           0.81700          4.01577          1.00011
   N           2.58935          2.29829         -0.59796
   H           2.84904          4.42203         -0.82183
   H           4.08341          3.57750          0.12804
   H           2.56861          3.25399          1.99035
   H           2.60075          4.96899          1.53188
   H           0.47380          3.06414          0.86809
   H           0.36014          4.35738          1.84512
   H           1.71776          2.38597         -1.13408
   H           3.28536          1.95210         -1.25677

60
DMT_3EDA_TS1 # E(6-31+G*)=-1259.61817794; E(ACCPVTZ//6-31+G*)=-1260.07404070 H
   N          -3.59946          1.75279          0.70005
   C          -4.05463          1.41218          2.06139
   C          -4.00639         -0.09306          2.31326
   N          -2.62581         -0.56477          2.52225
   H          -2.64967          1.40513          0.53182
   H          -3.46863          1.91280          2.85150
   H          -5.09360          1.75177          2.16045
   H          -4.57789         -0.31266          3.22409
   H          -4.51610         -0.60107          1.47589
   H          -2.04286         -0.37329          1.69923
   H          -2.62871         -1.57710          2.64348
   H          -3.56526          2.76701          0.60164
   C          -0.14936         -0.18523         -0.65327
   O          -0.80947          0.44626          0.27447
   C           0.60336         -1.46116         -0.18419
   H           0.01584          1.76866         -1.85352
   C           0.85729          4.29753         -2.93455
   C          -0.35932          3.47866         -3.36600
   N          -0.81094          2.58410         -2.26306
   N           0.57626          5.04022         -1.69784
   H           1.73292          3.63388         -2.84458
   H           1.07782          5.00748         -3.73876
   H          -1.18407          4.14440         -3.64032
   H          -0.11516          2.84977         -4.22743
   H          -1.10233          3.14880         -1.46264
   H          -1.61735          2.02251         -2.54327
   H           0.74953          4.43743         -0.88307
   H           1.20899          5.83384         -1.61672
   C           2.07074          1.18277         -0.70591
   C           1.85914          1.84518          0.65805
   N           0.80420          2.87349          0.62389
   H           2.55414          1.89608         -1.38424
   H           2.75800          0.33583         -0.57800
   H           1.65172          1.07371          1.41086
   H           2.80953          2.31973          0.93027
   H          -0.07935          2.35295          0.64505
   H           0.84097          3.41617          1.48694
   H           1.12042          0.25085         -2.25237
   O          -0.96214         -0.57118         -1.84222
   C          -2.14099         -1.29672         -1.51859
   H          -2.77678         -0.73159         -0.82857
   H          -2.67645         -1.45923         -2.45893
   H          -1.90428         -2.27422         -1.07273
   N           0.83334          0.73915         -1.40139
```

C	1.86082	-3.49044	-0.65982
C	1.17784	-2.35878	-1.09922
C	0.72878	-1.73248	1.18315
C	1.41007	-2.86386	1.63460
C	1.98540	-3.75421	0.71433
C	2.72160	-4.97453	1.14028
O	3.23643	-5.77621	0.37101
O	2.77048	-5.11894	2.47912
C	3.46631	-6.28041	2.97956
H	2.29870	-4.18062	-1.37436
H	1.07396	-2.18112	-2.16599
H	0.27724	-1.04563	1.89106
H	1.49381	-3.05690	2.69890
H	3.39192	-6.21270	4.06465
H	4.51202	-6.25987	2.66335
H	2.98743	-7.19316	2.61700

References

[S1] a) Katritzky A. R.; Cai, C.; Singh, S. K. *J. Org. Chem* **2006**, *71*,3775-3380. b) Dermer, O. C.; King, J. *J. Org. Chem* **1943**, *8*, 168.

[S2] Krijgsman, J.; Husken, D.; Gaymans, R. J. *Polymer* **2003**, *44*, 7043-7053.

[S3] a) Harashina, H.; Nakane, T.; Itoh, T. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 2184-2193. b) Lu, C. X.; Li, Q.; Pan, J. *J Polym. Sci. Part A: Polym. Chem.* **1985**, *23*, 3031.

[S4] a) Zinner, H.; Sych, G.; Ludwiy, W. *J. Prakt. Chem.* **1962**, *17*, 113. b) Li, H.; Liu, C.; Guo, G.; Zhou, X.; Zhang, J.; Shen, D.; Zhang, Z.; Xie, P.; Yu, S.; Zhang, R. *J. Polym. Chem. Part A: Polym. Chem.* **2002**, *40*, 3161-3170.

[S5] a) Walker, J. A.; Vause, C. A. *Sci. Am.* **1987**, *253*, 98. b) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.

[S6] IIieva, S.; Galabov, B.; Musaev, D. G.; Morokuma, K.; Schaefer III, H. F. *J. Org. Chem.* **2003**, *68*, 1496-1502.

[S7] Fukushima, K; Coulembier, O.; Lecuyer, J. M.; Almegren, H. A.; Alabdulrahman, A. M.; Alsewailem, F. D.; McNeil, M. A.; Dubois, P.; Waymouth, R. M.; Horn, H. W.; Rice, J. E.; Hedrick, J.L. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1273-1281.