Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

Controlled Radical Polymerisation of Methyl Acrylate Initiated by a Well-Defined Cobalt Alkyl Complex

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Includes:

- experimental data for X-ray structure determination of **1** and **2**
- synthetic procedures and characterisation data for **1** and **2**
- experimental procedures for polymerisation experiments
- graphs of polymer mass / polydispersity and kinetic plots for polymerisation experiments

Contents

Structure Determination of 2

Data Collection

A brown rod crystal of $C_{24}H_{27}CoN_2O_2$ having approximate dimensions of 0.12 x 0.14 x 0.60 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX II diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of 173.0 $\pm$ 0.1 K to a maximum 2θ value of 61.1°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 30.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

Of the 31367 reflections that were collected, 6288 were unique (R_{int} = 0.061); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 8.60 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[2]), with minimum and maximum transmission coefficients of 0.761 and 0.902, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[3]. The structure appears to be a case of whole-molecule disorder, wherein all of the atoms are disordered in two distinct orientations save for the Co which is common to both orientations. Prior to treating it as a disorder problem both twinning and pseudosymmetry were eliminated as possible causes for the extremely large anisotropic displacement parameters. Solving the structure in both $P2_1$ and Pn did nothing to resolve the original problem, i.e. that of the irregular geometry and non-positive definite anisotropic displacement parameters. In short, solving and refining in a lower symmetry space group generates all the problems associated with missed symmetry.

The merging R for space group $P2_1$ is 0.052, while the same for space group Pn is 0.054, the merging R for the chosen space group, $P2_1/n$, is 0.061. The disorder was treated by lowering the occupancies of each atom (one at a time) to 0.5 and refining. Residual peaks were then assigned to the second disordered fragment. Once two complete molecules had been assigned, the Shexl SAME instruction was used to maintain similar bond lengths and angles for each disordered fragment. In this way no one bond or set of bonds were restrained to any particular values (as would be the case if the AFIX 66 command were used to constrain 6 atoms to a hexagonal geometry); however, both fragments had to maintain similar geometries. Finally, pairs of atoms (i.e., C1 and C1', etc) were constrained to have equivalent anisotropic displacement parameters (using the EADP instruction for each pair of atoms in the molecule).

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions with only isotropic displacement parameters refined. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 6288 reflections and 365 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.125$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.139$$

The standard deviation of an observation of unit weight[5] was 1.18. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and –1.43 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf'' were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All refinements were performed using the SHELXL-97[10] via the WinGX[11] interface.

References

(1) SAINT. Version 7.60A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2009).
(2) SADABS. Bruker Nonius area detector scaling and absorption correction - V2008/1, Bruker AXS Inc., Madison, Wisconsin, USA (2008).
(3) SIR97 - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. (1999) J. Appl. Cryst. 32, 115-119.
(4) Least Squares function minimized:
$\Sigma w(F_o^2-F_c^2)^2$
(5) Standard deviation of an observation of unit weight:
$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$
where: N_o = number of observations, N_v = number of variables
(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
(10) SHELXTL Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA. (1997).
(11) WinGX – V1.70 – Farrugia, L.J.; J. Appl. Cryst., 32, 837 (1999).

Experimental Details

A. Crystal Data

Empirical Formula	$C_{24}H_{27}CoN_2O_2$
Formula Weight	434.41
Crystal Color, Habit	brown, rod
Crystal Dimensions	0.12 X 0.14 X 0.60 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 7.5525(2) Å b = 17.4630(6) Å c = 15.6446(5) Å $\alpha = 90^{o}$ $\beta = 96.808(2)^{o}$ $\gamma = 90^{o}$ V = 2048.8(1) $Å^3$
Space Group	*P* $2_1/n$ (#14)
Z value	4
D_{calc}	1.408 g/cm^3
F_{000}	912.00
μ(MoKα)	8.60 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker X8 APEX II
Radiation	MoKα (λ = 0.71073 Å) graphite monochromated
Data Images	1462 exposures @ 30.0 seconds
Detector Position	40.00 mm
$2\theta_{max}$	61.1^{o}
No. of Reflections Measured	Total: 31367 Unique: 6288 (R_{int} = 0.061)
Corrections	Absorption (T_{min} = 0.761, T_{max}= 0.902) Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0116P)^2+5.4874P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	6288
No. Variables	365
Reflection/Parameter Ratio	17.23

Residuals (refined on F^2, all data): R1; wR2	0.125; 0.139
Goodness of Fit Indicator	1.18
No. Observations ($I>2.00\sigma(I)$)	4667
Residuals (refined on F): R1; wR2	0.087; 0.127
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.53 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.43 $e^-/Å^3$

Experimental Procedures

Materials

All reactions were performed in an inert atmosphere glove box or on a vacuum line using standard air-sensitive techniques unless otherwise noted. Anaerobic anhydrous solvents (THF, diethyl ether, hexanes) were purified in Glass Contour solvent purification towers. Methyl acrylate (99% Aldrich) was dried over CaH_2, distilled under reduced pressure, freeze-pump-thaw degassed, and stored under dinitrogen at –35ºC after filtration through alumina. $CDCl_3$ (99.6+ atom% D) was dried over P_2O_5, distilled under reduced pressure, freeze-pump-thaw degassed, and stored under dinitrogen. V-70 (Wako) was stored at –35ºC under dinitrogen. 1-Phenyl-1,3-butanedione (99%, Aldrich), ethylenediamine (99% Aldrich), KOH (>90%, Aldrich), $Co(OAc)_2•4H_2O$ (>98%, Aldrich), and BEt_3 (1.0M in hexanes, Aldrich) were used as received.

Characterization methods

^{1}H NMR spectra were obtained in J Young NMR tubes in $CDCl_3$. NMR data were collected on a Varian 400MHz NMR spectrometer at room temperature. Chemical shift values were calibrated relative to residual $CHCl_3$, taken as 7.24 ppm. Magnetic moments were determined either in solution by Evans' method[1] in $CDCl_3$, using standard diamagnetic corrections.[2] Polymers were characterized by gel permeation chromatography (GPC), performed on a Polymer Laboratories PL-GPC 50+ with a PL-AS RT autosampler and PL-RI detector, a 5.0 μm PLgel guard column, and two PLgel 5 μm MIXED-C columns in series. The eluent was THF flowing at 1 mL/min at 30 °C. Polymer molecular weights were calculated against PS-H polystyrene standards (Polymer Laboratories).

Preparation of (bis(benzoylacetone)ethylenediiminato)cobalt (II) (1)

Complex **1** is prepared by a modification of a known procedure. [3] The bis(benzoylacetone)ethyl-enediamine proligand was prepared via the condensation of 1-phenyl-1,3-butanedione and ethylenediamine by refluxing in toluene using *p*-toluenesulfonic acid catalyst and a Dean-Stark trap in air. The diamine proligand (3.006 g, 8.63 mmol) was suspended in methanol (100 mL) and gently heated in air. KOH (0.9785 g, 17.44 mmol) was dissolved in minimal methanol and added dropwise to the stirring solution, followed by addition of $Co(OAc)_2•4H_2O$ (8.60 mmol). The mixture was heated 1 h, then cooled to room temperature to precipitate red-orange **1** (3.237 g, 92% yield). **1** was recrystallised from CH_2Cl_2/hexanes to yield red-orange needles for X-ray crystallographic analysis.
^{1}H NMR ($CDCl_3$ 25ºC) δ 24.7 (2H), 14.2 (2H), 7.7 (4H), 1.7 (4H), –20.7 (6H), –78.5 (2H); magnetic moment ($CDCl_3$): 1.99 μ_B; anal. calcd (found): C 65.19 (64.88), H 5.47 (5.58), N 6.91 (6.65).

(1) a) D. F. Evans, *J. Chem. Soc.* 1959, 2003-5. b) S. K. Sur, *J.Magn. Res.* 1989, **82**, 169-173.
(2) a) A. Earnshaw, in *Introduction to Magnetochemistry*, Academic Press, New York, 1968. b) C. J. O'Connor, *Prog. Inorg. Chem.* 1982, **29**, 203-83.
(3) a) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.* 1955, **77**, 5820-5824. b) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.* 1974, **96**, 392-400.

Preparation of (bis(benzoylacetone)ethylenediiminato)(ethyl)cobalt (III) (2)

BEt_3 (1.0M hexanes, 3.0 mmol) and **1** (1.0 mmol) were combined in THF (20 mL). Air (360 mL) was slowly introduced to the reaction mixture, which was stirred for 20 h, then filtered through silica in air. The filtrate was reduced to dryness, the brown residue triturated with hexanes, and the resulting brown solids collected by filtration to yield **2** as a brown powder (391 mg, 89% yield). **2** was recrystallised from Et_2O/hexanes to yield brown needles for X-ray crystallographic analysis.
^{1}H NMR ($CDCl_3$ 25ºC) δ 7.93 (m 4H), 7.35 (m 6H), 5.80 (s 2H), 3.56 (m 4H), 3.39 (q 2H), 2.13 (s 12H), –0.16 (t 3H). anal. calcd (found): C 66.36 (66.04), H 6.26 (6.33), N 6.26 (6.08).

Typical polymerization procedure

The appropriate cobalt reagent (0.050 mmol), methyl acrylate (2.25 mL, 25.0mmol), and an appropriate amount of V-70, were combined in toluene (2.75 mL) in a 50 mL thick-walled glass bomb and the mixture heated at 50ºC in an oil bath. Aliquots were removed at appropriate intervals via pipette and volatiles were removed under reduced pressure. Monomer conversions were determined gravimetrically and polymer mass data were determined by GPC.

Graphs for Polymerisation Experiment Data

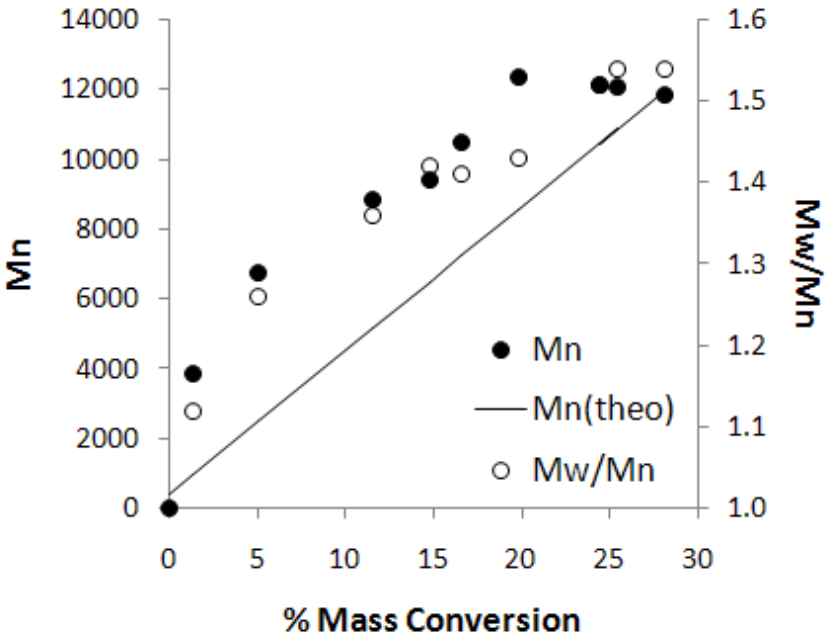

Figure 2. Variation of pMA mass (M_n) and polydispersity (M_w/M_n) with monomer conversion in toluene at 50ºC. $[\mathbf{1}]_i$:$[V\text{-}70]_i$:$[MA]_i$ = 1:0.6:500, $[\mathbf{1}]_i$ = 0.010 M.

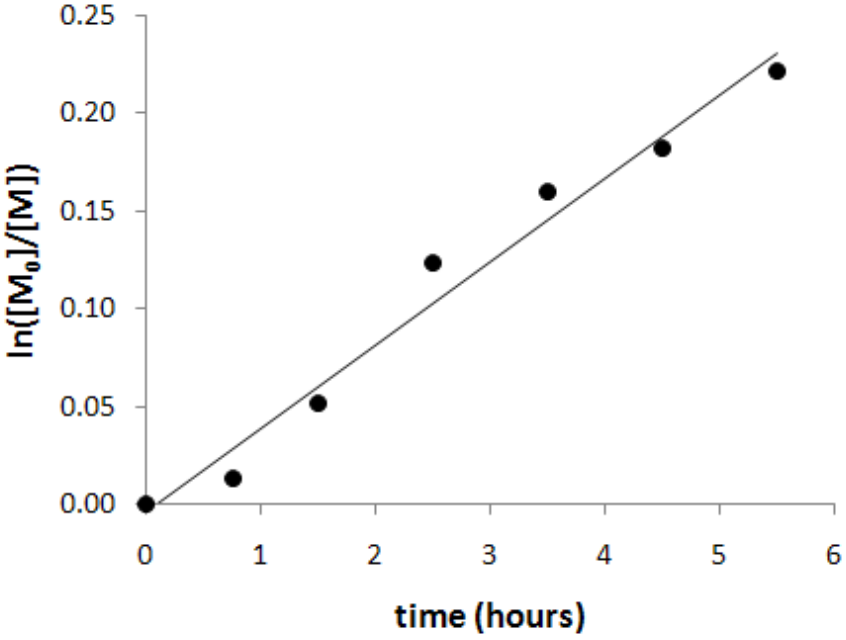

Figure 3. Kinetic plot for polymerization of MA with **1** and V-70 in toluene at 50ºC. $[\mathbf{1}]_i$:$[V\text{-}70]_i$:$[MA]_i$ = 1:0.6:500, $[\mathbf{1}]_i$ = 0.010 M.

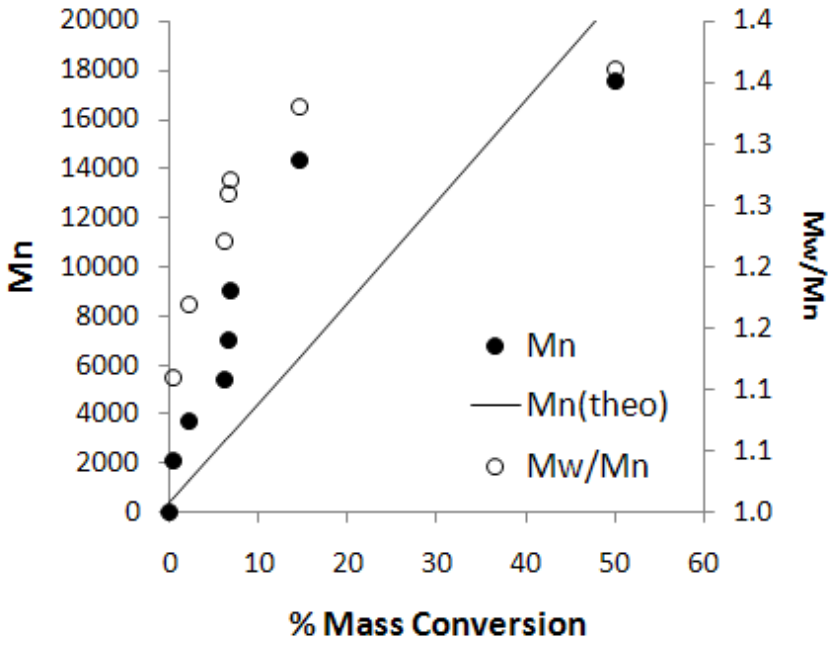

Figure S1. Variation of pMA mass (M_n) and polydispersity (M_w/M_n) with monomer conversion in toluene at 50ºC. $[\mathbf{1}]_i$:$[V\text{-}70]_i$:$[MA]_i$ = 1:0.9:500, $[\mathbf{1}]_i$ = 0.010 M.

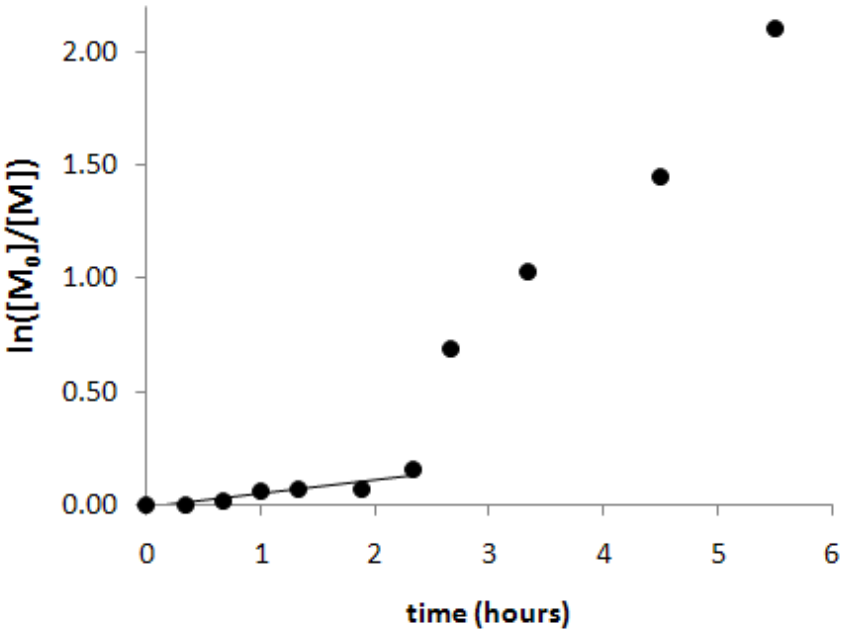

Figure 4. Kinetic plot for polymerization of MA with **1** and V-70 in toluene at 50ºC. $[\mathbf{1}]_i$:$[V\text{-}70]_i$:$[MA]_i$ = 1:0.9:500, $[\mathbf{1}]_i$ = 0.010 M.

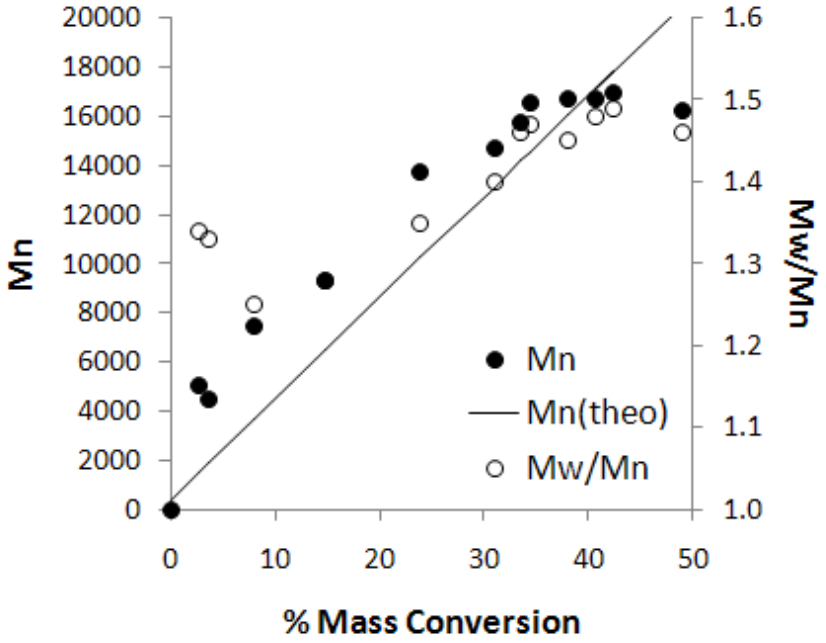

Figure S2. Variation of pMA mass (M_n) and polydispersity (M_w/M_n) with monomer conversion in toluene at 50ºC. $[\mathbf{2}]_i$:$[MA]_i$ = 1:500, $[\mathbf{2}]_i$ = 0.010 M.

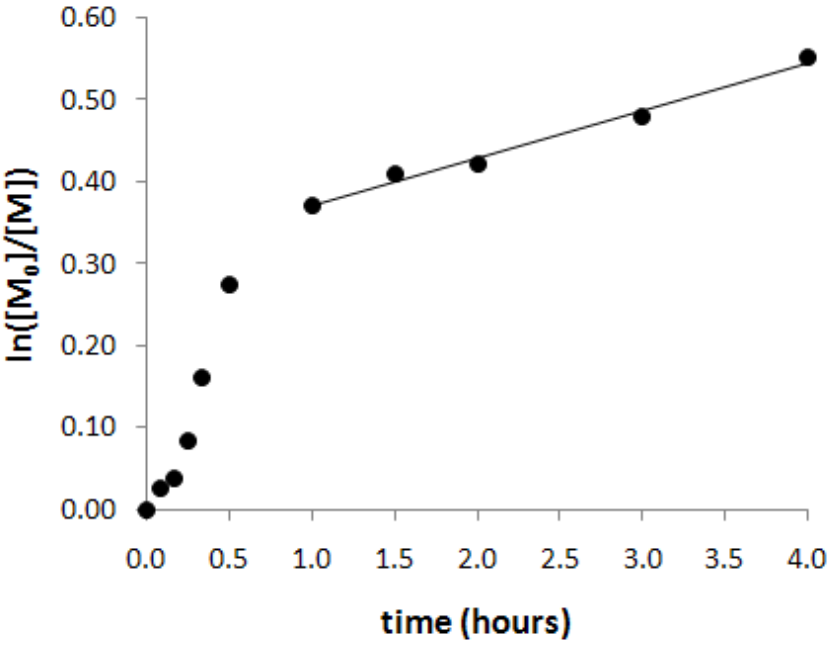

Figure 5. Kinetic plot for polymerization of MA with **2** in toluene at 50ºC. $[\mathbf{2}]_i$:$[MA]_i$ = 1:500, $[\mathbf{2}]_i$ = 0.010 M.

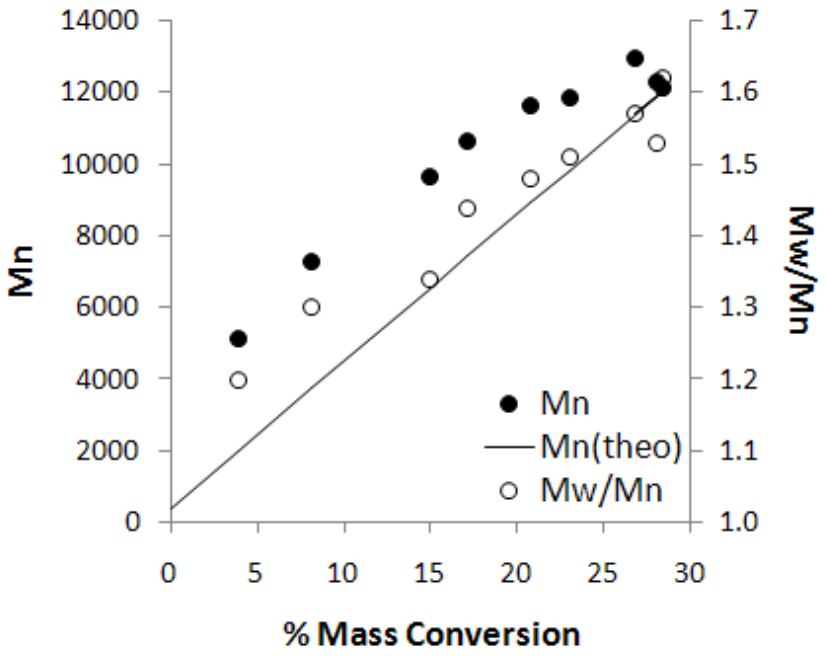

Figure S3. Variation of pMA mass (M_n) and polydispersity (M_w/M_n) with monomer conversion in toluene at 50ºC. $[\mathbf{1}]_i:[\mathbf{2}]_i:[MA]_i = 1:500$, $[\mathbf{1}]_i = 0.010$ M.

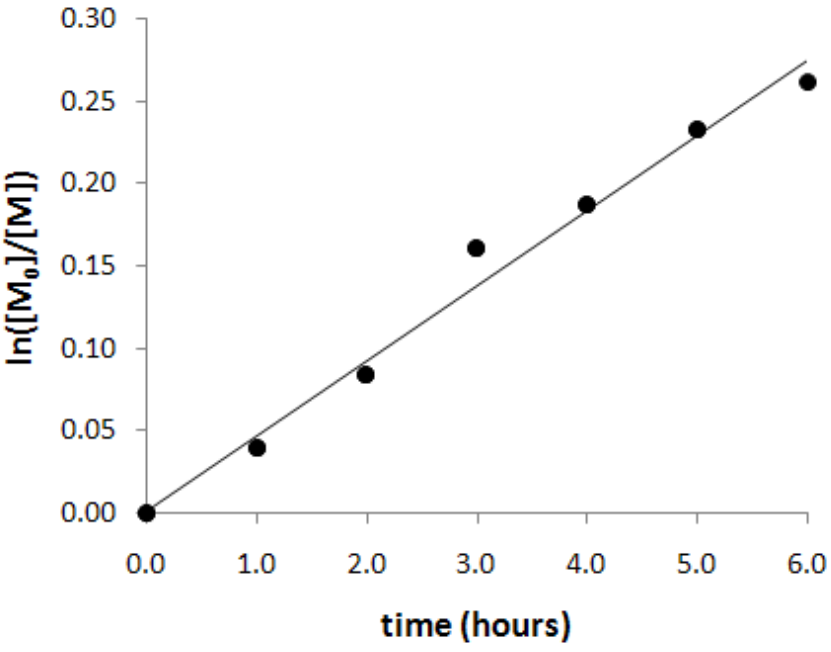

Figure 6. Kinetic plot for polymerization of MA with **1** and **2** in toluene at 50ºC. $[\mathbf{1}]_i:[\mathbf{2}]_i:[MA]_i = 1:500$, $[\mathbf{1}]_i = 0.010$ M.