Supporting Information

Highly Efficient Recyclable Hydrated-Clay supported Catalytic System for Atom Transfer Radical Polymerization

Selvaraj Munirasu[†], Ravi Aggarwal[‡], and Durairaj Baskaran[†,‡,*]

Division of Polymer Science and Engineering, National Chemical Laboratory, Pune 411 008, India and Department of Chemistry, University of Tennessee, 552 Buehler Hall, Knoxville, TN 37996

Experimental Section

Methods and Materials:

The reagents such as $CuBr_2$, N, N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), ethyl-2-bromoisobutyrate (BrEiB), toluene (HPLC grade) and dry anisole were purchased from Aldrich, USA and used after degassing under pure N_2. Monomers such as methyl methacrylate (MMA), benzyl methacrylate (BnMA) were purchased from Aldrich (USA) and passed through basic alumina column (Aldrich, USA) in order to remove the inhibitor. Sodium montmorillonite (Closite Na) (Na-clay) was obtained from Southern Clay Products (USA) and used as received.

Size exclusion chromatography (SEC) was performed using GPC-TQ instrument equipped with two detectors (UV and RI) and two 60 cm PSS SDV-gel columns: 1 x 10μ/100 Å, 1 x 10μ/linear: 10^2-10^6 Å. THF was used as eluent at the rate of 1 mL min^{-1}. The calibration of SEC was performed using polystyrene standards from PSS Germany. Atomic adsorption spectroscopy (AAS) was performed using GBC-Avanta instrument. For copper analysis, 327.4 nm wavelength with lamb current of 4.00 mAmp was used and the instrument was calibrated using 0.5, 5 and 10 ppm standard copper solutions. The WAXD experiments were performed using a Rigaku Dmax 2500 diffractometer equipped with a copper target and a diffracted beam monochromator (Cu Kα radiation with λ = 1.5406 Å) with a 2θ scan range of 2-10° at room temperature. FTIR spectrum was recovered in KBr pellet using GX Perkin Elmer spectrophotometer. PerkinElmer Lambda 950 UV/VIS spectrometer was used for the measurement of copper leaching and a known concentration of $CuBr_2$ (λ_{max} = 941 nm) and $CuBr_2$-PMDETA solution in DMSO was used for the calibration (λ_{max} = 716 nm).

Preparation of CuBr₂-PMDETA intercalated Na-clay:

[†]National Chemical Laboratory, Division of Polymer Science and Engineering, Pune, India.

[‡] Department of Chemistry, University of Tennessee.

* To whom correspondence should be addressed. E-mail:baskaran@utk.edu; Tel: (865)974-5583

In a 250 mL round bottom flask, 0.550 g of Cu(II)Br$_2$ (2.46 mmol) was charged with 100 mL of methanol. An equimolar amount of ligand, PMDETA, 0.427 g (2.46 mmol) was added to form a homogeneous catalyst complex solution. To this, 5.35 g of Na-clay was added and stirred for 30 min. The methanol was removed using rotary evaporator and the residue, a blue colored catalyst supported Na-clay, was dried in high vacuum for 1 h at room temperature. The blue colored catalyst supported Na-clay was characterized using XRD. XRD d-spacing: Na-clay = 12.44 Å and Na-clay-CuBr$_2$-L = 14.57 Å.

AGET ATRP of BnMA and MMA in anisole at room temperature in the presence CuBr$_2$-PMDETA loaded Na-clay:

AGET ATRP was performed under N$_2$ in a dry Schlenk tube. In a typical polymerization, 0.3168 g of blue colored clay-supported catalyst, CuBr$_2$-PMDETA-Na-Clay, (Cu^{II}/Clay = 0.10 ([Cu^{II}]/[Na$^+$]$_{clay}$ = 0.5) was taken in a Schlenk tube and the tube was tightly sealed with a rubber septum. Oxygen was removed from the tube by applying vacuum and then back-filled with nitrogen. To this, 5 mL of BnMA (29.5 mmol) and 5 mL of dry anisole were added under nitrogen using gas tight syringe. The reducing agent, sodium ascorbate (3 mg, [NaAsc]$_0$/[I]$_0$ = 0.25) in 60 μL of deionized water (H$_2$O/clay = 18 wt %) was added slowly under stirring. The immiscible water droplets slowly disappeared through hydration of clay. The heterogeneous mixture was stirred for 1 h. The blue color of the clay catalyst slowly changed to bluish green indicating the reduction of Cu(II)Br$_2$ to Cu(I)Br in the hydrated layers of the clay. Then, the initiator, ethyl-2-bromo isobutyrate (BrEiB) (0.059 mmol), was added via a gas tight syringe to commence the polymerization. The supernatant anisole appeared colorless during the polymerization. In one of the reaction, a small portion of supernatant was withdrawn for the analysis of copper presence by UV-vis spectroscopy (716 nm) which showed no or insignificant amount of copper in it.

After 4.5 h, the reaction tube was opened and exposed to air to quench the reaction. The polymerization solution was diluted with 20 mL of toluene and stirred for 30 min in air. The catalyst loaded Na-clay was filtered using 0.45 μm Teflon membrane and the polymer in the colorless filtrate was recovered either by evaporation of solvent or precipitation in excess n-hexane. The polymer was dried at 60° C under vacuum for 4 h. The monomer conversion was calculated on the basis of gravimetric yield. The Na-clay catalyst was washed with toluene to

remove any adsorbed polymer. The recovered CuBr$_2$-PMDETA-Na-clay catalyst was collected and dried. SEC analysis of the poly(benzyl methacrylate) showed, $M_{n.SEC}$ = 55,800 g/mol and M_w/M_n = 1.26.

Recycling experiments: The recovered CuBr$_2$-PMDETA-Na-clay catalyst was taken in a Schlenk tube under nitrogen, and reagents such as BnMA (5 mL) and anisole (5 mL) were added in to it. After degassing the solution, additional ligand, PMDETA (6 μL) and an optimum amount of aqueous solution containing sodium ascorbate (2 mg, $[NaAsc]_0/[I]_0$ = 0.17, in 60 μL of deionized water (H$_2$O/clay = 18 wt %) was added slowly under stirring. After 1 h, ethyl-2-bromo isobutyrate (BrEiB) (0.059 mmol), was added via a gas tight syringe to commence the polymerization. The polymerization was terminated after 4.5 h by exposing to air and diluted with toluene. The PBnMA and the CuBr$_2$-PMDETA-Na-clay catalyst were recovered as described above.

Kinetics of BnMA polymerization: Kinetics of the BnMA polymerization was performed using 272 mg of CuBr$_2$-PMDETA-Na-Clay, (Cu^{II}/Clay = 0.10) which was dried at 30°C for 1 h under vacuum. Anisole (10 mL), BnMA (10 mL), and 2.2 mg of sodium ascorbate in 41 uL water were used for the polymerization. Polymerization was performed as described above using 6.61 x 10^{-5} mol of BrEIB. A small amount (~ 0.2 mL) of supernatant was withdrawn at regular intervals for the determination of monomer conversion and molecular weight using gas chromatography and SEC, respectively.

Table S1: Effect of hydration on clay supported catalyst for AGET atom transfer radical polymerization of BnMA (M)[a)] using ethyl-2-bromoisobutyrate (I) as initiator in anisole at 30°C. $CuBr_2$-L-Na-clay = 257 mg and Cu^{II}/clay = 0.10, [M]/[I]/[Cu^{II}]/[L] = 289/1/2/2[b)]

Run	H_2O/Clay wt %[c]	[NaAsc]/[I] %[d]	time h	conv.[e] %	$M_{n,th}$[f] $\times 10^{-3}$ g/mol	$M_{n,SEC}$[g] $\times 10^{-3}$ g/mol	M_w/M_n[g]
1	4.7	7.5	21.0	-	no polymerization		
2	4.7	15.0	21.0	32.1	17.4	45.9	1.32
3	9.4	15.0	3.0	38.6	19.6	51.1	1.28
4	14.1	15.0	2.0	33.6	17.1	42.5	1.45

a) monomer ([M] = 2.95 mol/L) was polymerized in 1:1 v/v in anisole using [I] = 5.9 × 10^{-3} mol/L, b) mole ratios of reagents, L = PMDETA, Cu^{II} = $CuBr_2$, c) amount of water with respect to Na-clay, d) concentration of sodium ascorbic acid with respect to initiator, e) determined by gravimetric yield, f) $M_{n,th}$= grams of monomer/[I]) × conv., g) determined by SEC using PS standards.
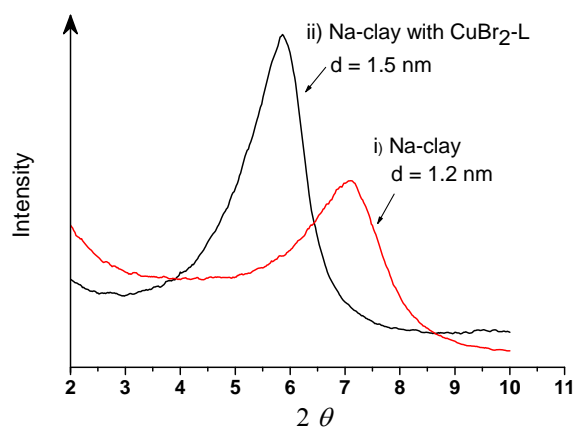

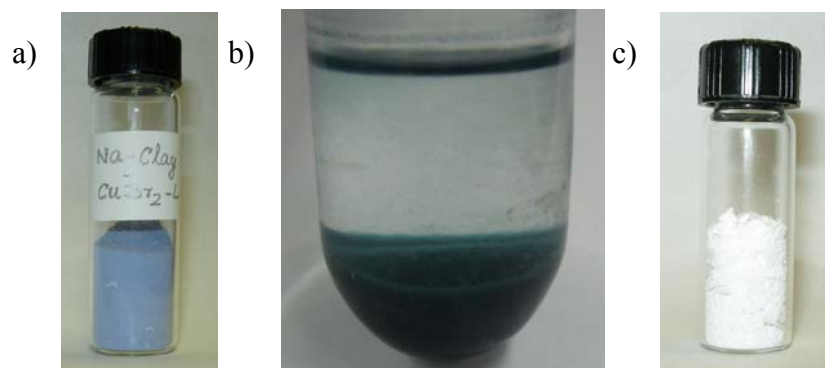**Figure S1**: XRD of Na-clay and $CuBr_2$-L intercalated Na-clay.

Figure S2: a) Blue colored CuBr$_2$-L supported Na-clay, b) Colorless anisole during BnMA polymerization over bluish-green colored catalyst on the hydrated Na-clay support at 30 ^{o}C, and c) Colorless PBnMA sample precipitated from the reaction mixture after filtration to remove the support.
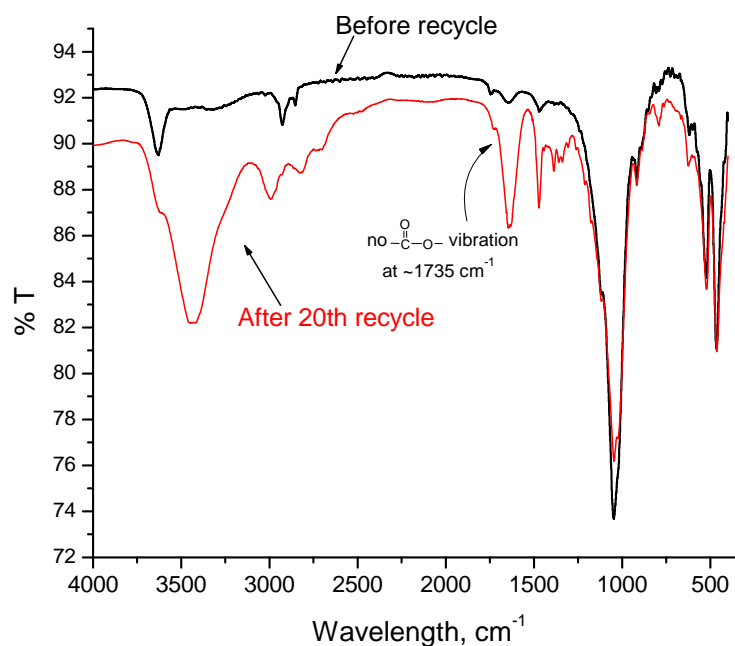

Figure S3: The FT-IR of the recovered catalyst loaded clay before and after 20 times recycled for the polymerization showing absence of intercalated polymer in it.
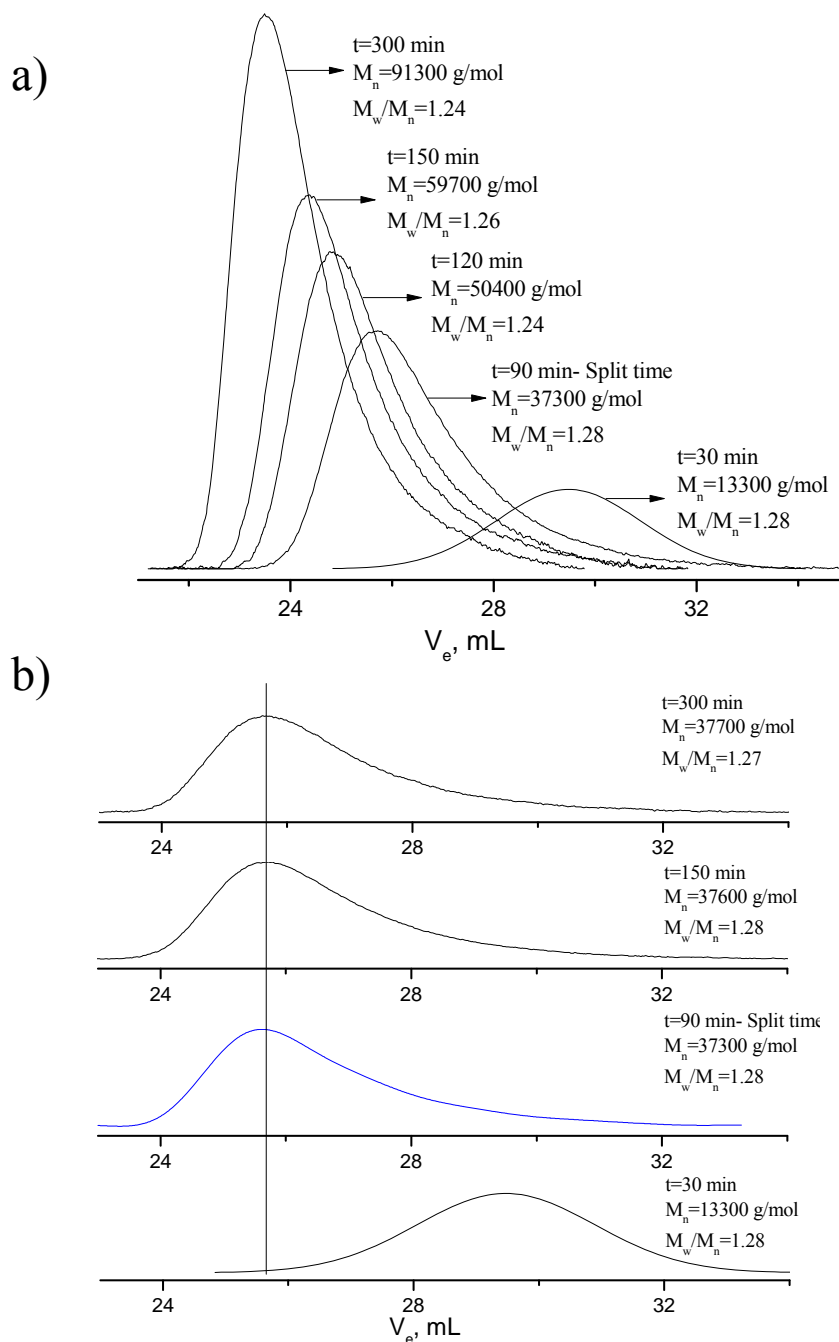
Figure S4: SEC traces of polymers synthesized in split kinetics in anisole using hydrated $CuBr_2$-PMDETA loaded Na-clay (272 mg, Cu^{II}/clay = 0.10), [M] = 2.95 mol/L, [I] = 3.3×10^{-3} mol/L, $[NaAsc]_0/[I]_0 = 0.17$ a) progress of polymerization over supported catalyst and b) progress of polymerization after filtering the supported catalysts (solid line is to guide only to show no polymer growth).
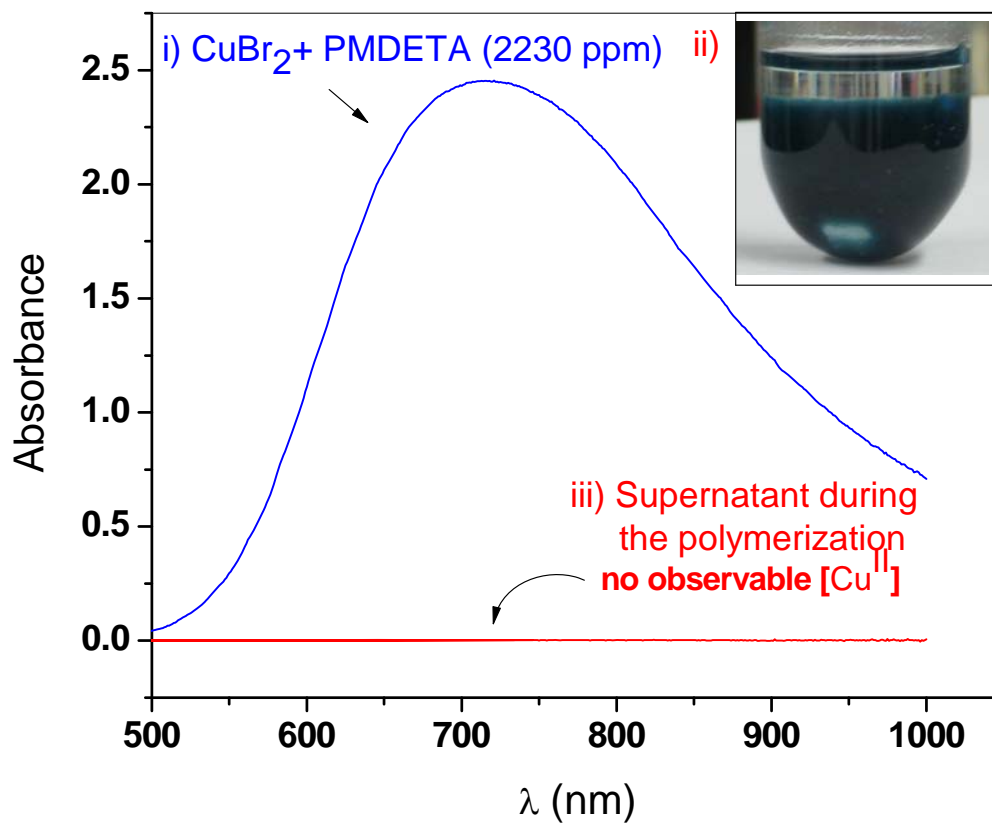
Figure S5: UV-Vis absorbance of CuBr$_2$-L complex, i) standard solution of CuBr$_2$ in DMSO, ii) supernatant anisole solution mixed with DMSO showing no or insignificant copper concentration.

Table S2: Characteristic data on the recycling of $CuBr_2$ intercalated hydrated Na-MMT (clay) catalyst for the AGET-ATRP polymerization of benzylmethacrylate using ethyl-2-bromoisobutyrate as initiator and sodium ascorbate as reducing agent in anisole at 30 ºC.

M/I//C^{II}/L mole ratio = 500/1/2/2, Na-MMT/$CuBr_2$/L_m (support) = 0.317 g with 0.12×10^{-3} mol of $CuBr_2$, [BnMA] = 2.95 mol/L (50 % v/v), [BrEiB] = 5.89×10^{-3} mol/L, and [$CuBr_2$-PMDETA]$_0$/[BrEiB]$_0$ = 2.

Number of recycle	Ligand (µL)	Na Asc-H_2O (mg-µL)	time, t	conv.[a] %	$M_{n,th}$[b] g/mol	$M_{n,SEC}$[c] g/mol	M_w/M_n[c]	$f =$ $M_{n.th}/M_{n.SEC}$	Cu ppm (AAS)
0	0	3-60	4.5	48	36550	55800	1.26	0.66	0.174[d]
2	4	3-60	8.0	34	25900	30300	1.31	0.86	-[e]
3	0	3-60	4.5	64	48700	53300	1.25	0.91	-[e]
4	0	2-60	4.5	21	16080	36100	1.25	0.45	-[e]
5	4	2-60	4.5	59	44900	46700	1.26	0.96	3.25[d]
6	4	1-60	18.0	47	35770	35900	1.15	0.99	-[e]
7	4	2-60	4.5	63	47900	43500	1.22	1.10	-[e]
8	4	2-60	4.5	60	45700	42200	1.20	1.08	4.74[d]
9	4	2-60	4.5	56	42600	40900	1.19	1.04	7.90[d]
10	6	2-60	4.5	62	47100	45800	1.22	1.03	2.52[d]
11	8	2-60	4.5	68	51700	50200	1.20	1.03	-[e]
12	6	2-60	4.0	65	49700	46100	1.42	1.08	-[e]
13	6	2-60	3.5	55	42100	52400	1.29	0.80	-[e]
14	6	2-60	3.0	54	40900	39000	1.29	1.05	-[e]
15	6	2-40	2.5	44	33800	30600	1.21	1.10	-[e]
16	6	2-40	2.0	54	41370	38200	1.35	1.08	-[e]
17	6	2-40	1.5	45	34570	35300	1.28	0.98	-[e]
18	6	2-40	1.0	40	30800	30800	1.35	1.00	-[e]
19	6	2-40	2.5	62	47200	44300	1.31	1.07	-[e]
20	6	2-40	10.0	94	71300	53900	1.29	1.32	9.37[d]
21	6	2-30	3.0	57	43000	54200	1.36	0.79	-[e]

a) determined by gravimetry, b) $M_{n,th}$ = [monomer]/[I]) × conv. × molecular weight of monomer, c) determined by SEC using PS standards, d) determined using atomic absorption spectroscopy (AAS), e) <0.02 ppm of polymer solution analyzed by UV-Vis in the presence excess ligand in DMSO and anisole at λ_{max} = 716 nm.