ELECTRONIC SUPPLEMENTARY INFORMATION

Natural catalyst mediated ARGET and SARA ATRP of N-Isopropylacrylamide and Methyl acrylate

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Materials and Methods:

Materials: N-Isopropyl acrylamide (NIPAM; Aldrich, 97%) was recrystallized three times from a mixture of toluene/ n-hexane (v/v) 1:1) prior to use. Methyl acrylate(99%,Aldrich), Ethyl 2-bromoisobutyrate, (99%,Aldrich) TREN(96%,Aldrich) were used as received. ME_6TREN was synthesized as per procedure. Mineral concentrate of drum stick leaves Green catalyst(GC) was extracted as per general wet digestion method. N,N-iimethylformamide (DMF) HPLC grade and other solvents of reagent grade, diethyl ether, acetone, tetrahydrofuran (THF), 2-propanol, methanol, and all other solvents are were purchased from Avra Chemicals India and used as received.

Characterization

Molecular weight and Đ value of polymers were determined using Gel Permeation chromatography (GPC). The GPC system was equipped with a JASCO PU-4180 RHPLC pump and Jasco RI-4030 refractive index detector using WTARES Styragel HR4E(DMF) 4.6 x 300 mm column with DMF as an eluent at a flow rate of 0.5mL/min at 50 °C. The apparent molecular weights (Mn) and Đ value were determined using linear PMMA (Mn = 2000-100000) standards using ChromNAV Ver.2 software.^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument. All Spectra were measured relative to Me_4Si (δ 0.0 ppm) or DMSO-d_6 residual peak (2.56ppm). GC-MS analysis of the methanolic extract of *Moringa Oleifera* and green catalyst were performed using Elite -5MS capillary column fixed to a Perkin Elmer clarus 680 placed with mass spectrometer Clarus 600(EI). Spectral analyses were done using Turbo mass version 5.4.2 software. XPS (X-ray photoelectron spectroscopy) measurement was done using XPS microprobe (PHI 5000 versa probe-ULVAC-PHI Inc).wide scan spectra were measured with a step size of 1.6 eV. The individual Cu2p, Fe2p, O1s and C1s spectra were collected at high resolution with a step size of 0.05 eV. Elemental analysis was performed on Inductively Coupled Plasma-Optical Emission Spectroscopy(ICP-OES) (Perkin-Elmer Optima 7000 DV, PerkinElmer Inc., Waltham, MA, USA).

Electrochemical Studies

All the electrochemical measurements were done on Biologic model SP-150 potentiostat controlled by EC lab software. A three-electrode system that comprises a glassy carbon electrode (5 mm dia), a Pt wire, and Ag/AgCl (3 M KCl) as working, counter and reference electrodes respectively was used for all the electrochemical experiments. Glassy carbon electrode was modified according to the procedure reported earlier. 10.0 ml of solution containing green catalyst (0.2ml), KNO_3 ($3.3x10^{-2}$)$molL^{-1}$ and HNO_3 (6.2 $x10^{-2}$) $molL^{-1}$ was used as the electrolyte solution. The metal ions initially were reduced to its zero oxidation state from their respective initial oxidation state and deposited on modified glassy carbon electrode by chronoamperometry method. The deposited metals were stripped out using linear sweep technique.

Extraction of Green catalyst (GC)

2.0 g of dried, finely powdered *Moringa oleifera* leaves was digested with 10ml of Con.HNO_3 until brown fumes cease, followed by cooling to room temperature. To this solution, 4ml of water, 7ml of hydrogen peroxide were added and heated to boil for about 7 minutes. The resultant extract(2.0ml) was then cooled to room temperature, filtered and used for polymerization.

Table S1 ICP-OES data of drumstick leaves extract

Entry	Element	Element wavelength in nm	Amount of element in ppm
1	Cu	327.393	0.761
2	Fe	238.204	2.469
3	Mg	285.213	46.81
4	Zn	206.200	0.661
5	Ca	317.933	35.15

Procedure for green catalyst mediated ARGET ATRP of NIPAM

Polymerization of NIPAM in 2-PrOH/H_2O (3:1, *v/v*) mixture of solvent was carried out at 30°C. Initially, NIPAM (0.500 g, 4.41mmol) and ascorbic acid (12mg, 0.06 mmol) were taken in a polymerisation tube equipped with a stir bar. The tube was closed with a rubber septum and was then degassed for about 15 minutes and backfilled with nitrogen for a total of five times. While purging nitrogen, 2-PrOH/H_2O (3:1, *v/v*) (total 2 ml), was added. Then 25 μL(0.76ppm of copper and 2.469 ppm of iron) of green catalyst followed by ME_6TREN (5mg, 0.02 mmol) were quickly added. Polymerization reaction was initiated by adding EBiB initiator(4mg, 0.02 mmol).To stop polymerization, rubber septum was opened and the polymerization mixture was exposed to air. The viscous liquid was then dissolved in 2ml of THF and precipitated in excess cold ether. The polymer was then dried under vacuum until a constant weight was reached. It was used for further analysis.

Procedure for green catalyst mediated SARA ATRP of NIPAM

Initially, NIPAM (0.500 g, 4.41mmol) and Cu(0) wire (dimension = 7 cm length; thickness 0.27 mm) were wound over magnetic stir bar. The tube was closed with a rubber septum and was then degassed for about 15 minutes and backfilled with nitrogen for a total of five times. While purging nitrogen, 2-Propanol/H_2O (3:1, *v/v*) (total 2 ml), was added. Then 25 µL(0.76ppm of copper and 2.469 ppm of iron) of green catalyst followed by Me_6TREN (5mg, 0.02 mmol) were quickly added. Polymerization reaction was initiated by adding EBiB initiator (4mg, 0.02 mmol).To stop polymerization, rubber septum was opened and the polymerization mixture was exposed to air. The viscous liquid was then dissolved in 2ml of THF and precipitated in excess cold ether. The polymer was then dried under vacuum until a constant weight was reached. It was used for further analysis.

Procedure for green catalyst mediated ARGET ATRP of MA

Polymerization of MA in DMSO (50%v/v) solvent was carried out at 30°C. Initially, MA (1.9 g, 22.07mmol), Ascorbic acid (50mg, 0.27 mmol) were added into polymerisation tube was equipped with a stir bar. The tube was closed a rubber septum and was then degassed for about 15 minutes and backfilled with nitrogen for about five times. While purging nitrogen into the polymer tube, 2ml DMSO was added then followed by 25µl (0.76ppm of copper and 2.469 ppm of iron) green catalyst followed by Me_6TREN (21 mg, 0.092mmol). The polymerization was initiated by adding EBiB initiator (18mg,0.092mmol).In order to stop the polymerization rubber septum was opened the polymer mixture was exposed to air. The viscous liquid was then dissolved in 2ml of THF and precipitated in excess cold methanol. To get poly(methacrylate) which was used for further analysis, after drying under vacuum.

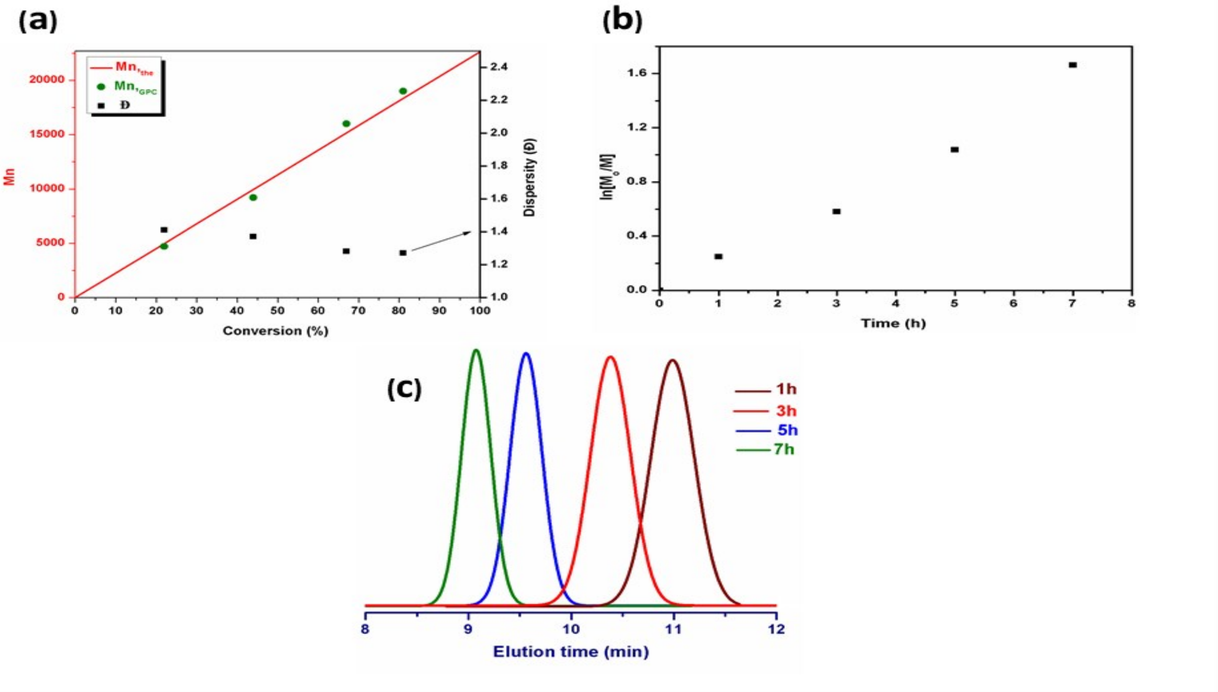

Figure S1(a) Dependence of M_n and Đ vs. Conversion in the polymerization of NIPAM in the presence of green catalyst at 30˚C: $[NIPAM]_0$:$[EBiB]_0$: $[Me_6TREN]_0$ $[AA]_0$= 200:1:1:3 (b) Kinetic plot of monomer conversion (c) GPC traces of PNIPAM obtained from kinetic studies.

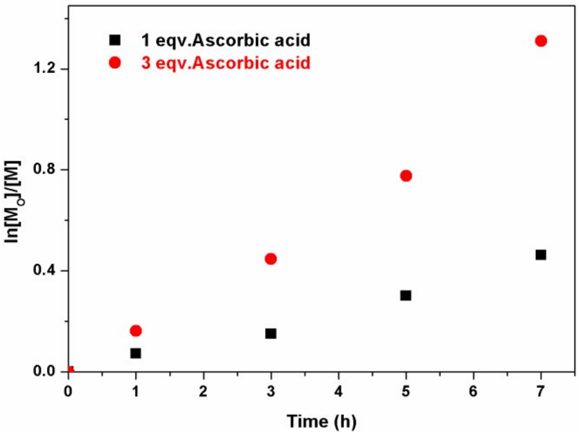

Figure S2 First order kinetic plots for different feed ratio of ascorbic acid in the ARGET ATRP of NIPAM under conditions:[NIPAM]/[EBiB]/[Me_6TREN]/[AA] = 200/1/1/1 or 3; green catalyst = 25µL; feed ratio of ascorbic acid 1 and 3 realtive to initiator concentration; solvent = 2-Propanol/H_2O (3:1, *v/v*) (total of 2 ml); Temperature = 30°C.

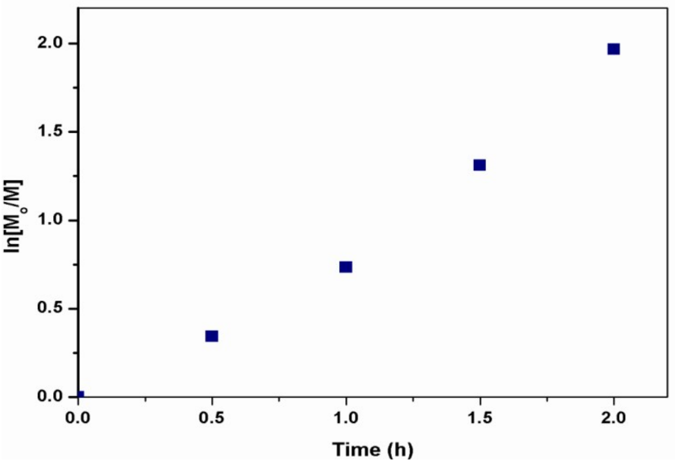

Figure S3 First order kinetic plots for the polymerization of NIPAM under SARA ATRP conditions:[NIPAM]/[EBiB]/[Me_6TREN] = 200/1/1, green catalyst = 25µL,reducing agent: Cu(0) wire (dimension = 7 cm length; thickness 0.27 mm) wound over magnetic stir bar . solvent = 2-Propanol/H_2O (3:1, *v/v*) (total of 2 ml); Temperature = 30°C.

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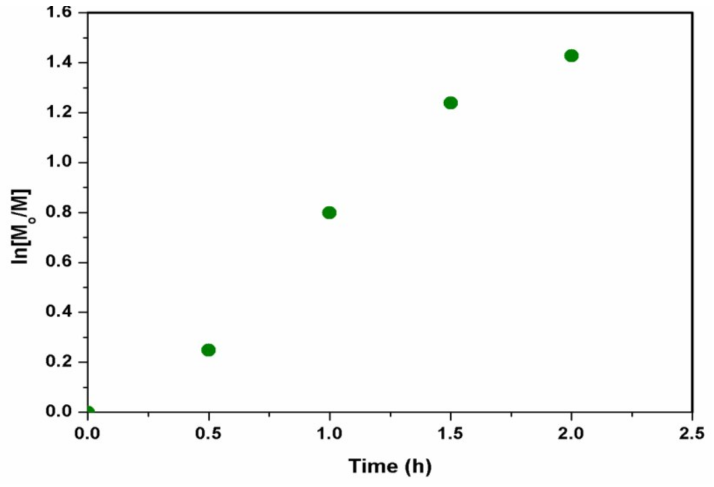

Figure S4 First order kinetic plots for the polymerization of Methyl acrylate under SARA ATRP conditions:[MA]/[EBiB]/[ME$_6$TREN]= 242/1/1; green catalyst = 25µL; reducing agent: Cu(0) wire (dimension = 7 cm length; thickness 0.27 mm) wound over magnetic stir bar; solvent = DMSO (2 ml); Temperature = 30˚C.

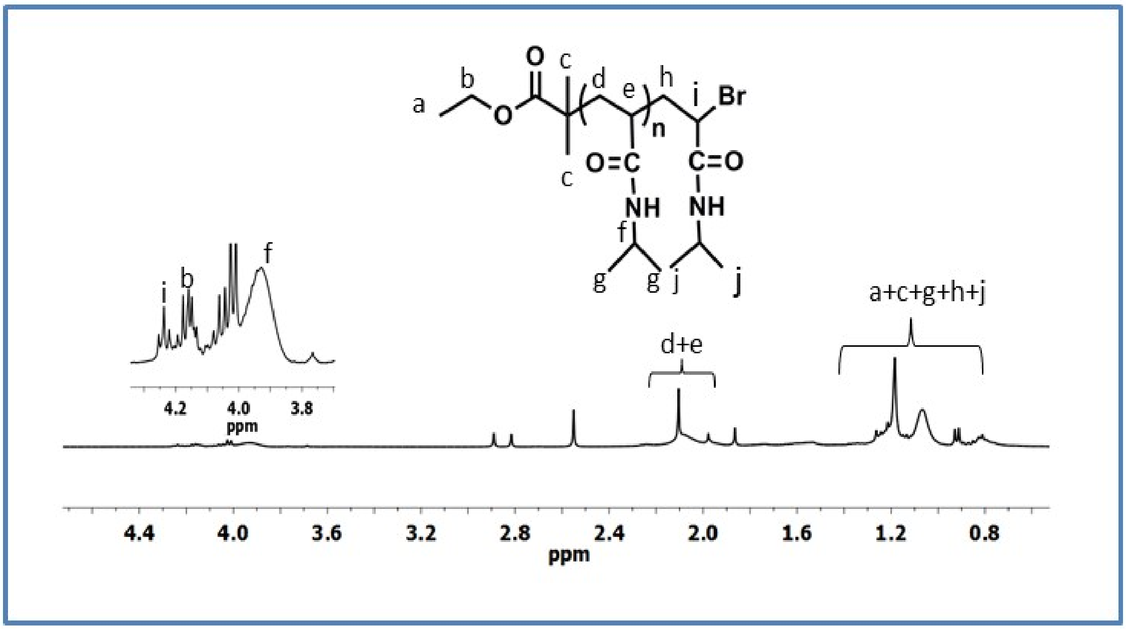

Figure S5 ^{1}H NMR of PNIPAM