Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Recoverable and recyclable nickel-cobalt magnetic alloy nanoparticle catalyzed reversible deactivation radical polymerization of methyl methacrylate at 25 °C

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Contents:

1- Materials. All reagents were used as received unless stated otherwise. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized based on published procedures.[1] Nickel(II) acetylacetonate ($Ni(acac)_2$, 95%, Aldrich), cobalt(II) acetylacetonate ($Co(acac)_2$, 97%, Aldrich), poly(vinylphenol) (PVPh, M_w ~11,000, Aldrich), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, reagent grade, N_2H_4 50-60%, Aldrich), methyl 2-bromopropionate (MBP, 98%, Aldrich), 2,2′-bipyridyl (bpy, 99%, Aldrich), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), and laboratory reagent grade methanol were purchased from Sigma-Aldrich. Methyl methacrylate (MMA, 99%, Aldrich), methyl acrylate (MA, 99%, Aldrich) and styrene (St, ≥ 99%, Aldrich) were purified by passing the monomer through a column filled with basic aluminum oxide (Aldrich) to remove the antioxidant/inhibitor and then bubbled with N_2 for 30 minutes before use. Dimethyl sulfoxide (DMSO, Merck, India), tetrahydrofuran (THF, Merck, India), chloroform ($CHCl_3$, Merck, India) and acetone was purified by distillation just before use in the polymerization. Xylene (Merck, India) was dried and purified by refluxing over sodium/benzophenone just before use. Deuterated chloroform ($CDCl_3$) used for NMR spectroscopy was purchased from Aldrich (purity > 99.8%). PVPh-Ni_3Co_1 alloy nanoparticles was prepared according to the published procedure.[2]

2- Experimental Procedures.

2.1. Representative procedure for Ni-Co alloy nanoparticles catalyzed RDRP of MMA.

A typical homopolymerization of MMA (P4, Table S1) was performed using Schlenk techniques under nitrogen atmosphere, as described in Scheme 1. The molar ratio of the reactants for this reaction is as follows: MMA:MBP:Ni-Co:PMDETA = 200:1:1:1. First, Ni-Co nanoparticle (0.015 g, 0.25 mmol) was placed in a Schlenk flask and was heated at 60 °C for 2 h under vacuum to remove any trapped moisture or any other gaseous entity and temporarily sealed with a silicone rubber septum. The flask was then purged by three vacuum-nitrogen cycles. Dry DMSO (2.6 mL), previously purged with dry nitrogen for 15 min, was then added to the flask using a dry syringe and was further purged with nitrogen for 15 min to remove any residual oxygen from the system. Me_6TREN (67 µ L, 0.25 mmol) and MBP (28 µL, 0.25 mmol) were then added to the mixture and was again purged with nitrogen for another 20 min. Then, degassed MMA (5.3 mL, 50.0 mmol) was then added to the flask by a syringe added under a nitrogen flow. The reaction mixture was again purged with nitrogen for another 20 min under magnetic stirring to ensure the removal of any trace of oxygen from the system. The flask was then permanently sealed with silicone rubber septum and placed in a silicone oil bath thermostated at 25 °C with constant magnetic stirring. After the specified reaction time, the polymerization was stopped via exposure to air. After the reaction, the DMSO was added to the reaction mixture to make the polymer soluble. The DMSO soluble polymer was precipitated twice from a chilled methanol. The purified polymer was then isolated by filtration, dried under vacuum (10^{-3} bar, 60 °C) for 12 h to obtain the solid polymer. The polymer was characterized by NMR spectroscopy and SEC. Same procedure was adopted for the polymerization of MA and St.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm of P4, Table S1, Fig. S3): 0.92 (–$C\underline{H_3}$ of PMMA, signal a); 1.77 (–$C\underline{H_2}$ of PMMA main chain, signal b), 3.55 (–$OC\underline{H_3}$ of PMMA, signal c).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm of P4, Table S1, Fig. S4); 17.90 (-$CH_2C(\underline{C}H_3)$ of PMMA); 44.66 (-$\underline{C}H_2$ of PMMA); 51.69 (–$O\underline{C}H_3$ of PMMA); 54.60 (-$O\underline{C}(CH_3)$ of PMMA); 178.02 (-$\underline{C}$=O of PMMA).

2.2. Kinetics study of Ni-Co alloy nanoparticles catalyzed RDRP of MMA. A series of experiments were carried out for the Ni-Co alloy nanoparticles catalyzed RDRP of MMA at 25 ^{o}C in DMSO using MBP as the initiator and they were stopped at different polymerization times (1.0 h to 24.0 h) to monitor (i) the conversion of MMA by gravimetry and (ii) the evolution of the molar masses and dispersities with time by means of SEC in THF. The data is summarized in Table S2.

2.3. Synthesis of PMMA with varying molecular weights. PMMA of varying molecular weights were synthesized using the protocol described in Section 2.1 just by varying $[\mathrm{MMA}]_0/[\mathrm{MBP}]_0$ ratio, keeping the amount of MBP and Ni-Co alloy nanoparticle constant.

2.4. Catalyst recyclability study of RDRP of MMA mediated by Ni-Co nanoparticle. After the reaction, DMSO was added to the reaction mixture to make the polymer soluble. The catalyst was isolated using a bar magnet and was washed thoroughly and dried. The purified/dried catalyst was then used again for the catalysis of same reaction under similar conditions. The reusability experiment of the catalyst was checked up to eight times in similar fashion. The data is summarized in Table 1.

3- Characterization.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra of the synthesized polymers were recorded at 25 °C on a Bruker 500 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal reference.

Size Exclusion Chromatography (SEC) Measurements. Molar masses (M_ns) and dispersities ($Đ$s) of the polymers were determined using a size exclusion chromatography (SEC) with triple-detection GPC (from Agilent Technologies) using a PL0390-0605390 LC light scattering detector capable of detecting at two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, and a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300 × 7.5 mm columns. THF was used as the eluent for this study at a flow rate of 1.0 mL min^{-1}. The entire SEC-HPLC system was thermostated at 35 °C during the entire duration of the measurement. Polystyrene standards were used to calibrate the SEC instrument. The results were processed using the corresponding Agilent software.

Transmission Electron Microscopic (TEM) Analysis. A drop of the Ni-Co alloy nanoparticles' suspension in ethanol was cast onto a carbon-coated copper grid and dried and imaged at an accelerating voltage of 200 kV under a JEOL high-resolution electron microscope (Model JEM 2010E).

4- Supplementary Tables.

Table S1. Optimization of the reaction parameters for the Ni-Co alloy nanoparticles catalyzed RDRP of MMA.[a]

Entry	Reaction condition	Time (h)	Conv. (%)	$M_{n,theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	MMA/MBP/Ni-Co/bpy/Xylene/90 ºC	48	47	9500	13600	1.44
P2	MMA/MBP/Ni-Co/PMDETA/Xylene/90 ºC	48	51	10400	12100	1.36
P3	MMA/MBP/Ni-Co/PMDETA/Xylene/105 ºC	48	52	10600	14700	1.39
P4	MMA/MBP/Ni-Co/Me_6TREN/DMSO/25 ºC	24	100	20200	21300	1.24
P5	MMA/MBP/Ni-Co/DMSO/25 ºC	48	0	-	-	-
P6	MMA/MBP/Me_6TREN/DMSO/25 ºC	48	0	-	-	-

Acronyms. MMA: methyl methacrylate; MBP: methyl 2-bromopropionate; bpy: 2,2′-bipyridyl; PMDETA: N,N,N′,N′′,N′′-pentamethyldiethylenetriamine; Me_6TREN: tris[2-(dimethyl-amino) ethyl]amine; DMSO: dimethyl sulfoxide. Catalyst = Ni-Co alloy; Ligand = Me_6TREN; Solvent = DMSO; Temperature = 25 °C. [a]Conditions: $[MMA]_0/[MBP]_0 = 200$; V_{MMA}: $V_{solvent}$ = 2:1. [b]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([MMA]_0/[MBP]_0 \times \text{yield} \times M_{MMA}) + M_{MBP}$, where M_{MMA} (= 100 g mol^{-1}) and M_{MBP} (= 167 g mol^{-1}) are the molecular weight of MMA and MBP, respectively. [c]Determined by SEC in THF, system was calibrated using polystyrene standards.

Table S2. Reaction conditions and results for the kinetics study of Ni-Co alloy nanoparticles catalyzed RDRP of MMA at 25 ºC in DMSO using MBP as the initiator.[a]

Entry	Time (h)	Conv. (%)	$M_{n,theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	1	5	1200	1500	1.35
P2	2	14	3000	3200	1.33
P3	4	33	6800	7400	1.32
P4	8	51	10400	11000	1.29
P5	15	75	15200	15900	1.25
P6	24	100	20200	21500	1.23

Acronyms. MMA: methyl methacrylate; MBP: methyl 2-bromopropionate; Me_6TREN: tris[2-(dimethylamino)ethyl]amine; DMSO: dimethyl sulfoxide. [a]Conditions: $[MMA]_0/[MBP]_0 = 200$; V_{MMA}: $V_{solvent}$ = 2:1. Catalyst = Ni-Co alloy; Ligand = Me_6TREN; Solvent = DMSO; Temperature = 25 °C. [b]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([MMA]_0/[MBP]_0 \times \text{yield} \times M_{MMA}) + M_{MBP}$, where M_{MMA} (= 100 g mol^{-1}) and M_{MBP} (= 167 g mol^{-1}) are the molecular weight of MMA and MBP, respectively. [b]Determined by SEC in THF, system was calibrated using polystyrene standards. [b]Determined by SEC in THF, system was calibrated using polystyrene standards.

Table S3. Reaction conditions and results of the Ni-Co alloy nanoparticles catalyzed RDRP of MMA to synthesize PMMA with varying molecular weights.[a]

Entry	$[MMA]_0/[MBP]_0$	Time (h)	Conv. (%)	$M_{n,theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	100	24	100	10200	12100	1.26
P2	200	24	100	20200	21300	1.23
P3	500	24	100	50200	54900	1.27
P4	1000	24	96	96200	94700	1.29
P5	1500	24	92	138200	129500	1.30

Acronyms. MMA: methyl methacrylate; MBP: methyl 2-bromopropionate; Me_6TREN: tris[2-(dimethylamino)ethyl]amine; DMSO: dimethyl sulfoxide. [a]Conditions: [V_{MMA}: $V_{solvent}$ = 2:1. Catalyst = Ni-Co alloy nanoparticles; Ligand = Me_6TREN; Solvent = DMSO; Temperature = 25 °C. [b]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([MMA]_0/[MBP]_0 \times \text{yield} \times M_{MMA}) + M_{MBP}$, where M_{MMA} (= 100 g mol^{-1}) and M_{MBP} (= 167 g mol^{-1}) are the molecular weight of MMA and MBP, respectively. [b]Determined by SEC in THF, system was calibrated using polystyrene standards. [b]Determined by SEC in THF, system was calibrated using polystyrene standards.

Table S4. Reaction conditions and results of the Ni-Co alloy nanoparticles catalyzed RDRP of MMA in presence of various initiators.[a]

Entry	Initiator	Time (h)	Conv. (%)	$M_{n,\ theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	MBP	24	100	20200	21100	1.23
P2	MBiB	24	100	20200	22500	1.22
P3	BEB	24	92	18600	17900	1.28

Acronyms. MMA: methyl methacrylate; MBP: methyl 2-bromopropionate; MBiB: Methyl α-bromoisobutyrate ; BEB : (1-bromoethyl)benzene; Me_6TREN: tris[2-(dimethyl-amino) ethyl]amine; DMSO: dimethyl sulfoxide. [a]Conditions: $[MMA]_0/[MBP \text{ or } MBiB \text{ or } BEB]_0$ = 200; V_{MMA}: $V_{solvent}$ = 2:1. Catalyst = Ni-Co alloy; Ligand = Me_6TREN; Solvent = DMSO; Temperature = 25 °C. [b]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([MMA]_0/[MBP]_0 \times \text{yield} \times M_{MMA}) + M_I$, where "I" represents initiator used, MBP or MBiB or BEB, M_{MMA} (= 100 g mol^{-1}), M_{MBP} (= 167 g mol^{-1}) M_{MBiB} (= 181 g mol^{-1}) M_{BEB} (= 185 g mol^{-1}) are the molecular weight of MMA, MBP, MBiB and BEB, respectively. [c]Determined by SEC in THF, system was calibrated using polystyrene standards.

Table S5. Reaction conditions and results of the RDRP of vinyl monomers catalyzed by Ni-Co alloy nanoparticle.[a]

Entry	Monomer	Time (h)	Conv. (%)	$M_{n,theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	MA	12	100	17200	19700	1.24
P2	MMA	24	100	20200	23100	1.23
P3	St	24	82	17700	15900	1.30

Acronyms: MA : methyl acrylate ; MMA: methyl methacrylate; St : styrene; MBP: methyl 2-bromopropionate; Me_6TREN: tris[2-(dimethylamino)ethyl]amine; DMSO: dimethyl sulfoxide. [a]Conditions: $[M]_0/[MBP]_0 = 200$; V_{MMA}: $V_{solvent}$ = 2:1; Catalyst = Ni-Co alloy; Ligand = Me_6TREN; Solvent = DMSO; Temperature = 25 °C. [b]Determined by SEC in THF, system was calibrated using polystyrene standards.

Table S6. Reaction conditions and results of the RDRP of MMA catalyzed by Ni-Co alloy nanoparticle in different solvent mixtures.[a]

Entry	Solvent	Time (h)	Conv. (%)	$M_{n,theo.}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	Đ[c]
P1	DMSO/THF	24	100	20200	22300	1.27
P2	DMSO/$CHCl_3$	24	100	20200	23500	1.31
P3	DMSO/acetone	24	100	20200	21100	1.32

Acronyms: MMA: methyl methacrylate; MBP: methyl 2-bromopropionate; Me_6TREN: tris[2-(dimethylamino)ethyl]amine; DMSO: dimethyl sulfoxide. [a]Conditions: $[MMA]_0/[MBP]_0 = 200$; V_{MMA}: $V_{solvent}$ = 2:1; V_{DMSO}: V_{THF} = 1:1; V_{DMSO}: V_{CHCl3} = 1:1; V_{DMSO}: $V_{acetone}$ = 1:1; Catalyst = Ni-Co alloy; Ligand = Me_6TREN; Temperature = 25 °C. [b]Determined by SEC in THF, system was calibrated using polystyrene standards.

5- Supplementary Fig.

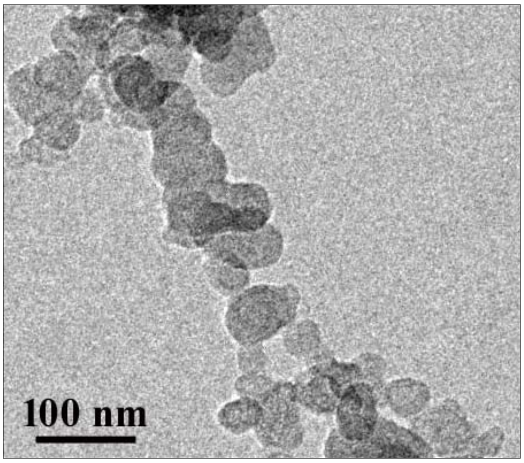

Fig. S1. TEM image of Ni-Co alloy nanoparticles.

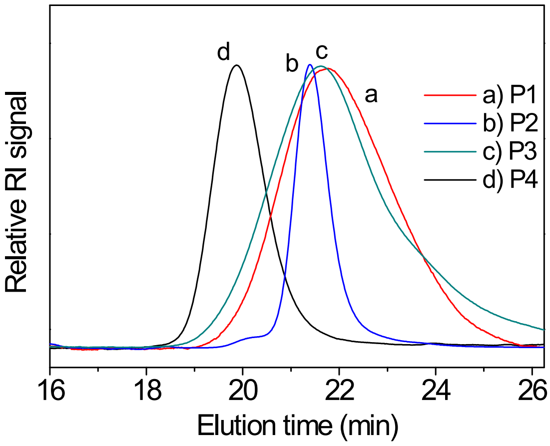

Fig. S2 SEC traces of the corresponding polymers (P1-P4, Table S1) obtained for the Ni-Co alloy catalyzed RDRP of MMA in presence of varying catalyst compositions (a) P1: MBP/Ni-Co/bpy/Xylene/90 ºC; (b) P2: MBP/Ni-Co/PMDETA/Xylene/90 ºC, (c) P3: MBP/Ni-Co/PMDETA/Xylene/105 ºC and (d) P4: MBP/Ni-Co/Me_6TREN/DMSO/25 ºC. Conditions: $[MMA]_0/[MBP]_0/[Ni\text{-}Co]_0/[bpy\ or\ PMDETA\ or\ Me_6TREN]_0 = 200:1:1:1$.

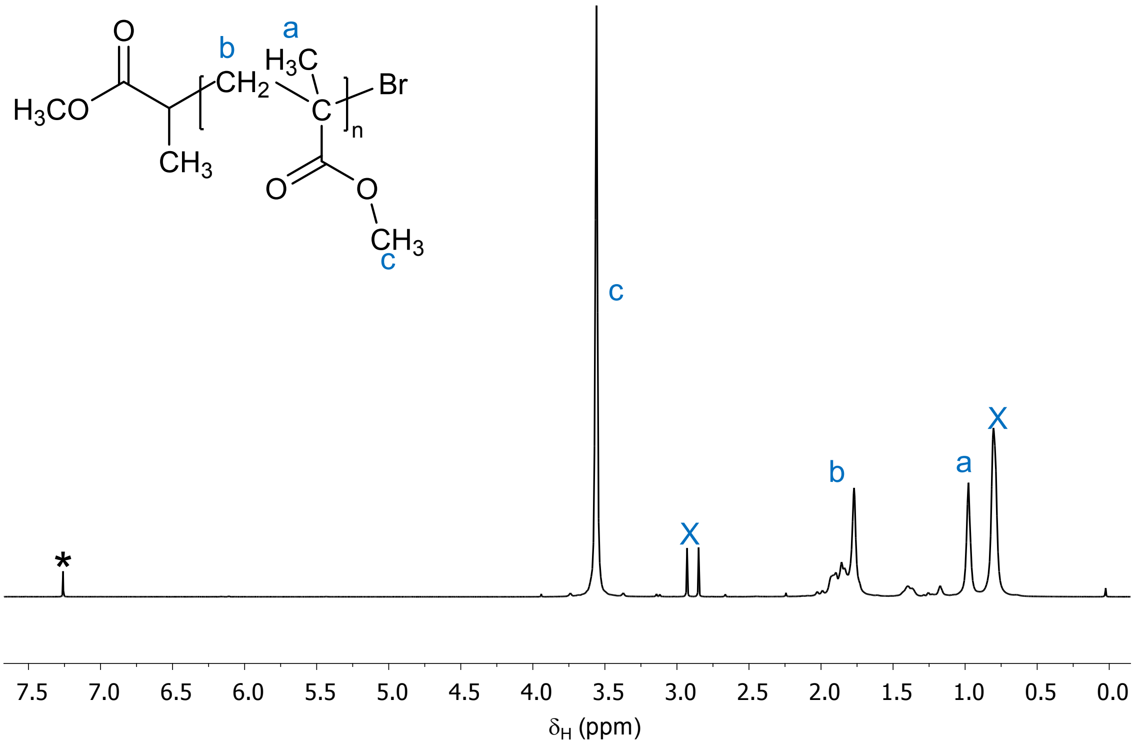

Fig. S3 ^{1}H NMR spectrum ($CDCl_3$, 20 °C) of PMMA (P4, Table S1) prepared by Ni-Co alloy catalyzed RDRP of MMA at 25 °C in DMSO using MBP as the initiator. (*) Solvent ($CHCl_3$) peak.

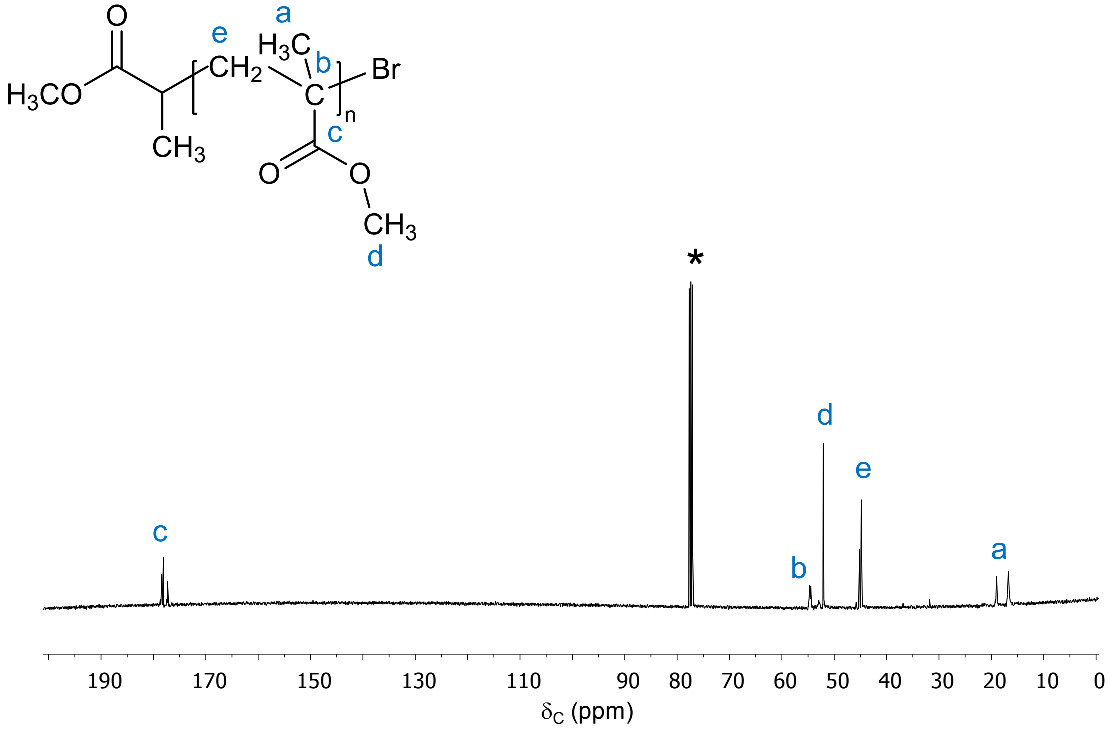

Fig. S4 ^{13}C NMR spectrum ($CDCl_3$, 20 °C) of PMMA (P4, Table S1) prepared by Ni-Co alloy catalyzed RDRP of MMA at 25 °C in DMSO using MBP as the initiator. (*) Solvent ($CHCl_3$) peak.

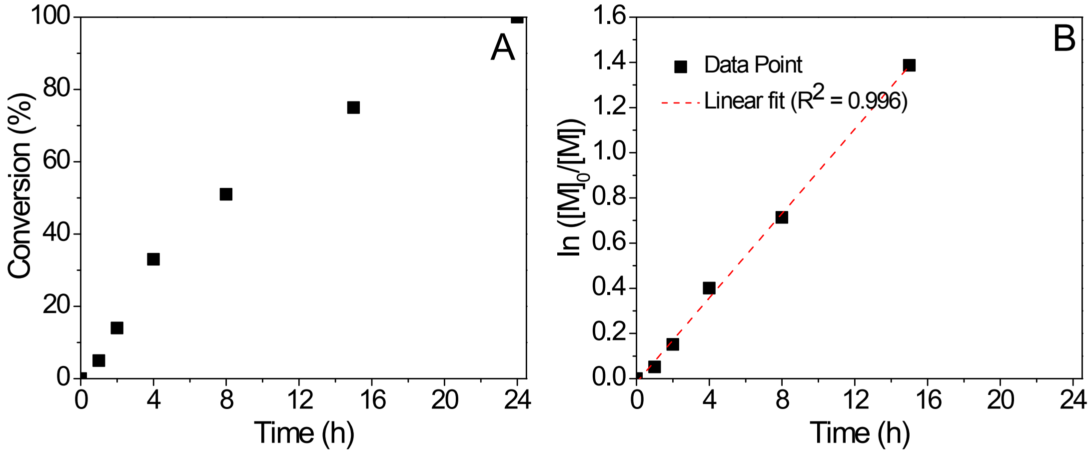

Fig. S5 Conversion *vs.* time (A) and ln[M]0/[M] *vs.* time (B) plots for the Ni-Co alloy catalyzed RDRP of MMA at 25 °C in DMSO using MBP as the initiator (P1-P6, Table S2).

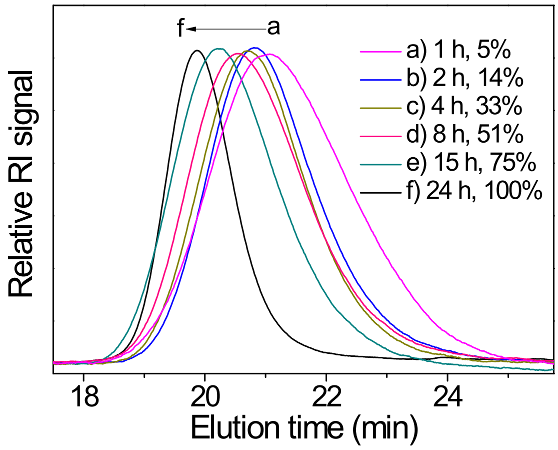

Fig. S6 Evolution of the SEC traces *vs.* time for the Ni-Co alloy catalyzed RDRP of MMA at 25 °C in DMSO using MBP as the initiator (P1-P6, Table S2).

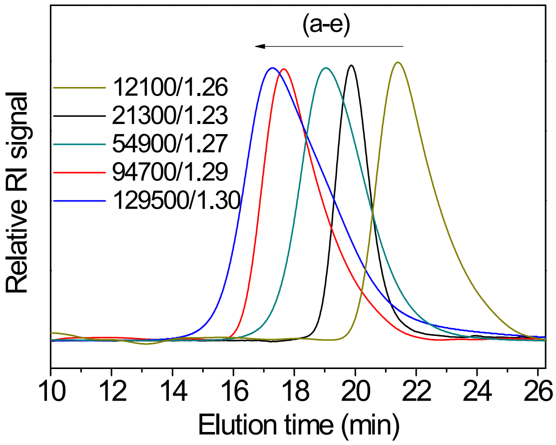

Fig. S7 Evolution of the SEC traces *vs.* $[MMA]_0/[MBP]_0$ ratio {a : 100, b : 200, c : 500, d : 1000, e : 1500} for the Ni-Co alloy catalyzed RDRP of MMA at 25 °C in DMSO using MBP as the initiator (P1-P5, Table S3).

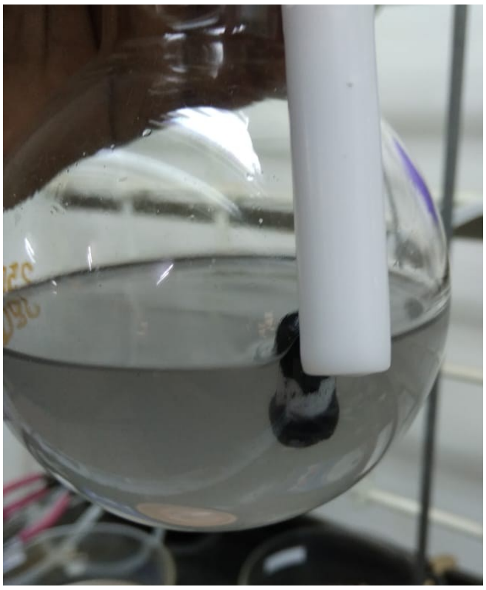

Fig. S8 Representative image showing catalyst recovery process using a simple bar magnet after completion of the polymerization reaction of MMA using Ni-Co alloy nanoparticles.

References

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