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Cyclic Amine Based Dithiocarbamate Chain Transfer Agents for the RAFT Polymerization of Less Activated Monomers[a]

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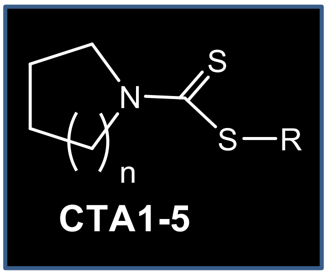
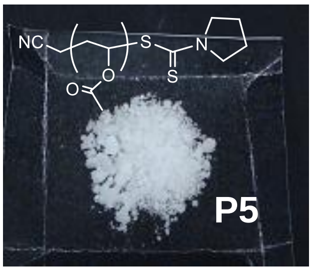
Summary

A series of new pyrrolidine, piperidine and imidazoline based dithiocarbamate chain transfer agents (CTAs) were synthesized and utilized to control the polymerization of different vinyl monomers especially the less activated monomers. The controlling ability of these dithiocarbamate CTAs depend on the presence of both activating and re-initiating groups and the monomer used. While pyrrolidine and piperidine based CTAs were reasonably good on controlling vinyl acetate polymerizations, the imidazoline based CTAs produce only oligomers. The living nature of the vinyl acetate polymerizations was studied by the kinetics and chain extension reactions and the end group fidelity was investigated by ^{1}H NMR and UV-visible spectroscopic techniques. Interestingly the vinyl acetate polymers synthesized using these pyrrolidine and piperidine based CTAs were almost colorless when precipitated and therefore were interesting by considering the industrial applications of these polymers.





Introduction

In recent years there is a great interest to use controlled or living radical polymerization (CRP/ LRP) techniques for the synthesis of well-defined and functional polymers. Reversible addition fragmentation chain transfer (RAFT) mediated polymerization is believed to be one of the most versatile CRP techniques[1] available to date for this purpose. The unavoidable attractiveness of the RAFT over the other CRP techniques for polymer chemists is mainly due to the simplicity of polymerization, tolerance towards different functional groups and the ability to polymerize wide variety of monomers. The controllability in RAFT is mediated by the addition of a chain transfer agent (CTA) during the polymerization which is otherwise a normal free radical polymerization (FRP). In general, four different classes of CTAs are used in RAFT process namely dithioesters, trithiocarbonates, xanthates and dithiocarbamates. Dithiocarbamates are one of the most interesting classes[2,3] of RAFT agents due to their ease of synthesis, ability to produce lesser colored and lesser odor polymer in comparison to other CTAs e.g. dithioesters. Dithiocarbamates are known to undergo delocalization of non-bonded electron pair of nitrogen atom with the thiocarbonyl group (C=S) which reduces the reactivity of C=S double bond towards the radical addition during the equilibrium stages of polymerization. This also leads to the reduced stability of macro-RAFT radicals and therefore useful to control the less activated monomers[1,3] e.g. vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP) etc. However, this delocalization of nitrogen loan pair can be manipulated by the placement of suitable functional group adjacent to the nitrogen atom[3-4] or by the addition of external stimuli e.g. acids.[5] This makes the dithiocarbamates suitable as universal or switchable CTAs for RAFT polymerization.[3-5] No other class of CTA is reported yet for this switchable behavior or universality.

Homopolymers and copolymers derived from less activated monomers such as vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP) have wide commercial applications in various coating, adhesives, dispersion systems, inks etc. These (co)polymers also have increased attention for biomedical applications by virtue of their biocompatibility. Poly(vinyl acetate) (PVAc) with controlled structures are extremely important in the context as a precursor to poly(vinyl alcohol) (PVA) for the ever increasing biomedical applications.[6] Very recently low molecular weight PVAc and its copolymers have also been recognized as one of the most CO_2-philic hydrocarbon materials to be used as surfactants in CO_2 medium.[7] RAFT is known to be one of the best techniques to control the polymerizations of VAc[3-6,7c-d,8] and NVP[9] which are otherwise very difficult to control.

Herein we report the synthesis of a series of novel pyrrolidine, piperidine and imidazoline based dithiocarbamate CTAs and their use to control the polymerization of different less activated vinyl monomers preferentially vinyl acetate. The effect of different activating and re-initiating groups toward polymerizations were investigated thoroughly. The controlling behavior of vinyl acetate polymerizations mediated by these CTAs was studied by kinetics, chain extension reactions and the end group fidelity was investigated by ^{1}H NMR and UV-visible spectroscopic techniques.

Experimental Part

Materials and characterizations

All chemicals were purchased from Sigma-Aldrich, Alfa Aesar or Merck. 2,2'-Azobisisobutyronitrile (AIBN) was obtained from HalloChem Pharm Co. Ltd. All monomers were purified by passing through neutral alumina column and stored in freezer before polymerizations. AIBN was purified by recrystallization from absolute alcohol.

NMR spectra were recorded on 400 MHz Bruker UltraShield AVANCE 400SB spectrometer. Residual solvent peaks were used as internal standard. Elemental microanalysis was performed using Eurovector E300 elemental analyzer. High resolution mass spectra were recorded on Agilent 6210 TOF/LCMS. The THF run SEC system was equipped with Waters 515 HPLC pump, 717plus autosampler, 2414 refractive-index detector. The following Styragel GPC columns were arranged in series: guard, HR5E (×2, 4.6mm ID × 300 mm), HR1 and HR0.5. The eluant flow rate was 0.3 mL/min and the columns were maintained at 40 ^{o}C. The DMF run SEC system was equipped with a Viscotek GPCmax Pump module, a Viscotek TDA 302 refractive index detector unit, fitted with TOSOH H_{HR} Guard Column and one TOSOH GMH_{HR}-M mixed bed column (5 μm, ID 7.8 mm × 300 mm). The eluent flow rate was 1.0 mL/min, and the columns were maintained at 60 °C. UV-visible spectra were recorded on SHIMADZU UV-2550 spectrophotometer.

Synthesis of different dithiocarbamate chain transfer agents

Synthesis of pyrrolidine based dithiocarbamate chain transfer agent, ***CTA1***

Pyrrolidine (1 g, 14 mmol) was slowly added by a syringe to a dispersion of NaH (60% in oil, 0.7 g, 10 mol% excess) in dry THF (20 ml) and stirred for a while at room temperature. The mixture was then heated at 60 ^{o}C for 2 h and cooled to room temperature before the careful addition of carbon disulfide (1.07 g, 14 mmol). The resultant solution was further stirred at room temperature overnight follwed by addition to distilled water (250 ml). Aqueous solution (60 ml) of $K_3Fe(CN)_6$ (4.629 g, 14 mmol) was then added dropwise to the earlier solution. The precipitate was filtered and dried at RT under high vacuum to produce light yellow solid (2.3 g). A part of the resultant solid (1.043 g, ~3.566 mmol) was then heated with excess AIBN (0.878 g, 5.349 mmol) under N_2 in ethyl acetate (30 ml) for 18 h. Solvent was removed in rotary evaporator and the product was purified by column chromatography using 2:3 EA/ hexane mixture to produce light yellow solid (1.2 g). Total yield 50%. ^{1}H NMR ($CDCl_3$): δ = 1.93 (s, 6H, 2×-CH_3), 1.99 (m, 2H, -CH_2), 2.08 (m, 2H, -CH_2-), 3.56 (t, 2H, -NCH_2-), 3.88 (t, 2H, -NCH_2-). ^{13}C NMR ($CDCl_3$): δ =

24.1, 26.3, 27.5, 41.6, 50.7, 54.2, 121.5, 186.9. MS: *m/z* = 237.04938 $[M+Na]^+$. $C_9H_{14}N_2S_2$: calcd. C 50.43, H 6.58, N 13.07, S 29.92%; Found C 50.02, H 6.46, N 12.88, S 30.74%.

CTA2, **CTA4** and **CTA5** were synthesized by a similar method as described for **CTA3** below.

Synthesis of dithiocarbamate chain transfer agent, ***CTA3***

Pyrrolidine (1 g, 14 mmol) was slowly added by syringe to a dispersion of NaH (60% in oil, 0.7 g, 10 mol% excess) in dry THF (30 ml) and stirred for a while at room temperature. The mixture was then heated at 60 ^oC for 2½ h. The light yellow mixture was cooled on ice bath before the careful addition of carbon disulfide (1.07 g, 14 mmol). The resultant mixture was then stirred at RT for ½ h and at 60 ^oC for 1 h. Methyl 2-bromoisopropionate (2.349 g, 14 mmol) was then added and the resultant mixture was refluxed at 65 ^oC for 18 h. The final solution was added to distilled water (250 ml) and the product was extracted by ether (250 ml). The solution was dried over anhydrous $MgSO_4$ and ether was removed in a rotary evaporator. The product was then purified by column chromatography using 30% EA in hexane to yield light orange liquid (2.65 g). Total yield 81%. ^1H NMR ($CDCl_3$): δ = 1.58 (d, 3H, -CH_3), 1.95 (m, 2H, -CH_2-), 2.06 (m, 2H, -CH_2-), 3.60 (m, 2H, -NCH_2-), 3.73 (s, 3H, -OCH_3), 3.88 (t, 2H, 2×-NCH_2-), 4.83 (q, 1H, -C*H*(CH3)-). ^{13}C NMR ($CDCl_3$): δ = 17.1, 24.3, 26.1, 48.3, 50.6, 52.8, 55.1, 172.8, 190.4. MS: *m/z* = 256.04402 $[M+Na]^+$. $C_9H_{15}NO_2S_2$: Calcd. C 46.32, H 6.48, N 6.00, S 27.48%; Found C 46.52, H 6.48, N 5.94, S 27.64%.

CTA2: Yield 77%. ^1H NMR ($CDCl_3$): δ = 1.28 (t, 3H, -CH_2C*H_3*), 1.73 (s, 6H, 2×-CH_3), 1.93 (m, 2H, 2×-CH_2-), 2.05 (m, 2H, 2×-CH_2-), 3.59 (t, 2H, 2×-NCH_2-), 3.83 (t, 2H, 2×-

NCH_2-), 4.2 (q, 2H, -OCH_2-). ^{13}C NMR ($CDCl_3$): δ = 14.1, 24.3, 26.1, 26.4 50.75, 54.0, 54.5, 61.8, 173.9, 190.0. MS: *m/z* = 284.07618 $[M+Na]^+$. $C_{11}H_{19}NO_2S_2$: Calcd. C 50.54, H 7.33, N 5.36, S 24.53%; Found C 50.59, H 7.42, N 5.32, S 24.44%.

CTA4: Yield 90%. ^{1}H NMR ($CDCl_3$): δ = 2.01 (m, 2H, 2×-CH_2-), 2.12 (m, 2H, 2×-CH_2-), 3.65 (t, 2H, 2×-NCH_2-), 3.93 (t, 2H, 2×-NCH_2-), 4.23 (s, 2H, -CH_2-). ^{13}C NMR ($CDCl_3$): δ = 22.1, 24.2, 26.2, 50.7, 55.8, 116.1, 187.5. MS: *m/z* = 209.01823 $[M+Na]^+$. $C_7H_{10}N_2S_2$: Calcd. C 45.13, H 5.41, N 15.04, S 34.42%; Found C 45.18, H 5.36, N 15.02, S 35.31%.

CTA5: Yield 93%. ^{1}H NMR ($CDCl_3$): δ = 1.73 (b, 6H, 3×-CH_2-), 3.83 (b, 2H, 2×-NCH_2-), 4.23-4.27 (b, 4H, 2×-NCH_2- and -CH_2CN). ^{13}C NMR ($CDCl_3$): δ = 22.8, 24.1, 25.9, 26.1, 51.8, 54.0, 116.2, 190.2. MS: *m/z* = 223.03365 $[M+Na]^+$. $C_8H_{12}N_2S_2$: Calcd. C 47.97, H 6.04, N 13.98, S 32.01%; Found C 48.26, H 6.04, N 14.04, S 32.78%.

*Synthesis of imidazoline based dithiocarbamate chain transfer agent, **CTA6***

2-Methyl-2-imidazole (0.1 g, 1.189 mmol) and K_3PO_4 (0.252 g, 1.189 mmol) were mixed and stirred in acetone (5 ml) for 5 min. Carbon disulfide (0.272 g, 3.566 mmol) was added slowly and stirred for 15 min at room temperature. Ethyl 2-bromopropionitrile (0.215 g, 1.189 mmol) was then added and the mixture was stirred further for 20 h at RT. Then the mixture was filtered, the solvent was removed and the crude was purified using 75% ethyl acetate in hexane to yield yellow liquid (0.262 g). Yield 84.6%. ^{1}H NMR ($CDCl_3$): δ = 1.29 (3H, t, -CH_2CH_3), 1.61 (3H, t, -CHCH_3), 2.67 (3H, s, -CCH_3), 3.83 (2H, t, -NCH_2-), 4.2 (4H, m, -NCH_2- and -OCH_2-), 4.59 (1H, q, -SC*H*CH_3). ^{13}C NMR ($CDCl_3$): δ = 14.1, 16.7, 21.2, 49.3, 52.2, 52.9, 61.9, 158.59, 171.7, 192.7. MS: *m/z* = 283.05496 $[M+Na]^+$. $C_{10}H_{16}N_2O_2S_2$: Calcd. C 46.13, H 6.19, N 10.76, S 24.63%; Found C 43.75, H 5.88, N 11.14, S 25.54%.

Synthesis of imidazoline based dithiocarbamate chain transfer agent, ***CTA7***

2-Methyl-2-imidazole (0.5 g, 5.944 mmol) and K_3PO_4 (1.262 g, 5.944 mmol) were mixed and stirred in acetone (30 ml) for 5 min. Carbon disulfide (1.357 g, 17.832 mmol) was added and stirred for ½ h at room temperature. Bromoacetonitrile (0.713 g, 5.944 mmol) was added and the resultant mixture was stirred further for 1½ h (with aluminium foil covering) at room temperature. Acetone was removed in rotary evaporator and the product was dried further at room temperature under high vacuum to produce bright yellow solid product (1.2 g). This product seemed to be sensitive to light or heat. This product was not purified further and used immediately for the polymerization reaction. Yield 95%. ^{1}H NMR ($CDCl_3$): δ = 2.67 (3H, s, -CH_3-), 3.88 (2H, t, -NCH_2-), 4.12-4.18 (4H, m, -NCH_2- and -CH_2CN). ^{13}C NMR ($CDCl_3$): δ = 20.9, 22.8, 52.5, 52.6, 115.3, 158.1, 188.5. MS: *m/z* = 222.01208 $[M+Na]^+$.

Typical RAFT polymerization of vinyl acetate (VAc) using ***CTA4 (P5)***

VAc (2 ml, 0.0216 mol), AIBN (3.6 mg, 2.169×10^{-5} mol), CTA4 (40.4 mg, 2.169×10^{-4} mol) and anisole (5 drops as internal standard) were mixed and transferred to a 25 ml Schlenk tube. The solution was degassed with three freeze-pump-thaw cycles using N_2 and brought to room temperature and then heated to 70 ^{o}C in nitrogen atmosphere for required time. The polymerization was stopped by cooling down the mixture to room temperature and exposing to air. Polymer was analysed by GPC(THF) as obtained without any purification. For end group analysis study polymer was precipitated from excess hexane before drying in vacuum oven at 60 ^{o}C for 18h.

*Typical synthesis of poly(vinyl acetate)-block-poly(vinyl benzoate), PVAc-b-PVBz (**P20**) by chain extension reaction*

This di-block copolymer was synthesized in a two step process. All polymers were analysed by GPC(THF) as obtained without any purification.

Step I: VAc (1.5 ml, 16.29×10^{-3} mol), CTA4 (15.15 mg, 8.136×10^{-5} mol), AIBN (1.34 mg, 8.136×10^{-6} mol) (VAc:**CTA4**:AIBN = 200:1:0.1) and 5 drops of anisole (as internal standard) were mixed and taken into a 25 ml Schlenk tube. The solution was then degassed by three freeze-pump-thaw cycles using N_2 and heated at 70 ^{o}C in nitrogen atmosphere for 7 h. A small portion of polymer was collected for NMR and GPC studies. Rest of the sample was dried under high vacuum for 2 h to produce a sticky whitish solid. Resultant polymer (**P20a**) (conversion 75.2%): $M_{n,Theor}$ 13130; $M_{n,GPC}$ 13960; PDI 1.41.

Step II: PVAc synthesized was mixed thoroughly with vinyl benzoate, VBz (2 ml), AIBN (1.5 mg) and anisole (5 drops as internal standard). The solution was then degassed by three freeze-pump-thaw cycles and heated at 70 ^{o}C in nitrogen atmosphere for 22 h. Resultant copolymer (**P20b**) $M_{n,GPC}$ 32460; PDI 1.76.

Results and Discussion

Synthesis of different dithiocarbamate chain transfer agents, CTA1-7

There are many acyclic and cyclic dithiocarbamates as chain transfer agents for the RAFT polymerizations are reported in the literature.[1-5] However the synthesis of pyrrolidine, piperidine and imidazoline based dithiocarbamate chain transfer agents (Figure 1) and their use for RAFT polymerizations are not reported yet. Dithiocarbamate **CTA1** (Scheme 1) were synthesized by two step reactions, at first synthesising pyrrolidine based bis(thicarbonyl) disulfide by oxidative coupling using potassium hexacyanoferrate(III) from respective thiocarbonyl-thio salt followed by the refluxing of bis(thicarbonyl)disulfide with AIBN[4] at 70 °C. **CTA2-7** were synthesiszed by reacting the corresponding thiocarbonyl-thio salts with appropriate alkyl bromide in an one pot methodology,[4a,10] (Schemes 1 and 2). All CTAs except **CTA7** were purified by column chromatography before characterizing by ^{1}H and ^{13}C NMR spectroscopic techniques, elemental microanalysis and high resolution mass spectrometry and stored in a refrigerator before use. **CTA7** was used as obtained from the reaction and used immediately. **CTA1-5** were also characterized by UV-vis spectroscopy in THF. All these CTAs showed characteristics π-π* absorption maxima at 276-282 nm and 235-247 nm corresponding to the thiocarbonyl-thio group (Figure 3).

Polymerization of vinyl acetate (VAc) using different CTAs synthesized

Controlling vinyl acetate (VAc) polymerization is a difficult task because of the lower stability of the propagating polymer radicals which leads to very fast polymerization reaction. Atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP) techniques are not very effective for this purpose. Revarsible addition fragmentation chain transfer (RAFT) mediated polymerization has unique advantages in this regard. Certain xanthates and dithiocarbamates are reported to be successful for VAc polymerization,[3-6,7c-d,8] because of the reduced C=S double bond character by oxygen or nitrogen lone pair conjugation respectively which slower the propagating polymer chain-CTA adduct formation and also partially due to the lower stabilization of the adduct which leads to the speeding up of the fragmentation of reinitiating radical both in the pre-equilibrium and main-equilibrium stages of polymerization reactions.[3] Initially we attempted to synthesize relatively low molecular weight poly(vinyl acetate) (PVAc) with the composition of VAc:CTA:AIBN = 100:1:0.1. Dithiocarbamates **CTA1-4** (Figure 1) were different in their re-initiating ('R') functionality with having same pyrrolidine activating ('Z') group. This will provide the efficieny of polymerization by the different pyrrollidine based dithiocarbamate CTAs of different re-initiating 'R' groups. Where as **CTA5-7** were synthesized with different 'Z' groups but having similar 'R' group as **CTA1-5**. From the VAc polymerization results it was observed that the controlling efficiency depended on both the 'Z' and 'R' group of the CTAs. All the pyrrolidine and piperidine based CTAs (**CTA1-5**) were, in general, moderately efficient to control the polymerization of vinyl acetate (VAc) (Table 1) with respect to the moleculat weight ($M_{n,GPC}$) and polydispersity index (PDI) achieved. Noteworthy to mention that the polymerization of VAc without using any CTA (**P1** in Table 1) produced very high molecular weight polymer with broad polydispersity (>2.9) within a very short period of polymerization. Among all pyrrolidine based CTAs, **CTA1** having cyanoispropyl re-initiating group yielded very less PVAc (**P2** in Table 1) even after longest polymerization time and the correlation between theoritical to GPC molecular weight and polydispersity index value achieved were inferier. All other pyrrolidine based CTAs (**CTA2-4**) were good in controlling the VAc polymerizations (**P3-P5** in Table 1) and the molecular weight ($M_{n,GPC}$) obtained were matching well with the theoritical values ($M_{n,Theor}$). The polydispersity index (PDI) of the polymers synthesized were moderately low (1.6-1.5). In general, PDI values for the VAc polymerizations using different pyrrolidine based CTAs were dependent on the re-initiating 'R' group present in the CTA as $-CH_2CN < -CH(CH_3)CO_2Me < -C(CH_3)_2CO_2Et < -C(CH_3)_2CN$. Among four pyrrolidine based CTAs used in this study, **CTA4** produced best results with respect to both $M_{n,GPC}$ and PDI values. It was indeed possible to synthesize relatively high molecular weight PVAc with moderately low PDI using **CTA4** (**P6** in Table 1). Polymerization of VAc using piperidine based **CTA5** (**P7** in Table 1) provided marginally improved polymers in terms $M_{n,GPC}$ and PDI in comparison to using **CTA4** (**P5** in Table 1) under similar conditions. This was most probably due to the relatively easier conjugation of nitrogen loan pair because of the lower ring strain in piperidine than in pyrrolidine.

The polymerization of VAc mediated by **CTA4** (with VAc:**CTA4**:AIBN = 350:1:0.1) demonstrated that polymerization proceeded via pseudo-first order kinetics (Figure 4a) and the monomer conversion increased with time like a typical living polymerization system. However the GPC results (Figure 4b) exhibited that there was a sudden increase in molecular weight at the initial stage of polymerization which followed linearly like a living polymerization system at higher conversions.

The imidazoline based agents, **CTA6-7** produced only oligomers after 24h of polymerization reaction of VAc (**P8** and **P9** in Table 1).

Polymerization of other vinyl monomers using the dithiocarbamate RAFT agents synthesized

The dithiocarbamates, **CTA1** and **CTA2** were ineffective in controlling polymerization of more activated monomers such as methyl methacrylate (MMA) and styrene (St) (**P10** and **P12** in Table 2) as reported before for the acyclic *N,N*-disubstituated dithiocarbamates.[4a] However Benaglia et. al recently reported that pyridinyl dithiocarbamates were highly effective to control the polymerization of more activated monomers when protonated.[5]

However our attempts to control the polymerization of MMA and St (**P11** and **P13** in Table 2) mediated by **CTA1** and **CTA2** in presence of strong acids were unsuccessful. This is not really unexpected as the nitrogen loan pair of pyrrolidine group in these agents is conjugated with the thiocarbonyl group making the nitrogen less basic in compare to the nitrogen in pure pyrrolidine. Polymerization of more activated monomers auch as MMA and St using imidazoline based **CTA6** and **CTA7** were not performed since these agents were not very stable at room temperature especially **CTA7**.

Polymerization of *N*-vinylpyrrolidone (NVP) (**P15-18** in Table 2) using **CTA1-4** showed some control over molecular weight but no significant control was observed with respect to the polydispersity. The control experiment of NVP polymerization without using any CTA produced very high molecular weight polymer just in 1h (**P14** in Table 2). The poor control in NVP polymerizations mediated by these dithiocarbamate CTAs was may be due to the different side reactions involved in the polymerization reactions[11a] or due to the presence minute amount of impurities. [11b] We do not have any further reasons to offer to explain this.

The polymerization of vinyl benzoate (VBz) (**P19** in Table 2) using **CTA4** provided some control with respect to both molecular weight and polydispersity.

Copolymers of vinyl acetate using CTA4 and end group analysis of resultant polymers

The living nature of the VAc polymerization mediated by dithiocarbamate **CTA4** was further confirmed by the synthesis of di-block copolymers by chain extension reactions and by the end group analysis of resultant homo- and di-block copolymers. The bulk polymerization of VAc in the presence of **CTA4** with the composition of VAc:CTA:AIBN = 200:1:0.1 at 70 °C for 7h produced PVAc with 75% conversion. After the removal of excess monomer by applying high vacuum for 2h produced almost colorless polymer (**P20a**, Scheme 3) of $M_{n,GPC}$

13960 and PDI 1.41 ($M_{n,Theor}$ 13130). The ^{1}H NMR spectrum of **P20a** confirmed the presence of dithiocarbamate end functional group. The methylene units of pyrrolidine group appeared at 2.15, 2.35, 3.6 and 3.9 ppm (Figure 6i) as in **CTA4** (Figure 1). However in this case resonances were broad due to the attachment of the pyrrolidine group with the long polymer chain. The presence of **CTA4** derived dithiocarbamate end functional group was further proved by the UV-visible spectroscopy. The absorption maximum at 278 nm corresponding to the π-π^* transition of dithiocarbamate group was observed in the UV-visible spectrum of **P20a** (Figure 7) where as such maximum was absent for the polymer synthesized without using any CTA (**P1** in Table 1).

Our initial attempt of chain extension reaction of **P20a** with NVP was unsuccessful. However the chain extension of **P20a** with vinyl benzoate (VBz) at 70 ^{o}C for 22h produced poly(vinyl acetate)-*block*-poly(vinyl benzoate), PVAc-*b*-PVBz copolymer (**P20b** in Scheme 3) of $M_{n,GPC}$ 32460 and PDI 1.76. The ^{1}H NMR spectrum of **P20b** also showed the presence of dithiocarbamate end functional group which appeared at 2.15, 2.35, 3.6 and 3.9 ppm (Figure 6ii). Again the absorption maximum at 279 nm corresponding to the π-π^* transition of dithiocarbamate group was observed in the UV-visible spectrum of **P20b**. The maximum at 235 nm for the copolymer **P20b** was mainly due to the absorption of benzoate side group present in the VBz repeat units of PVAc-*b*-PVBz copolymer.

Appearance of dithiocarbamate CTAs and vinyl acetate (co)polymers obtained

Dithiocarbamates are known for the lesser colored nature in compare to other RAFT agents[3] like dithioesters or trithiocarbonates etc. Indeed all thiocarbamates synthesized here were pale yellow solid or liquid and were almost colorless in solution (see supporting information). Therefore PVAcs synthesized using **CTA1-5** were very light yellow in color and produced nearly colorless solid when precipitated from hexane (Figure 8 and see supporting information). This avoids any post-polymerization treatment for the use of these polymers in color related applications.

Conclusion

Five pyrrolidine based, one piperidine based and two imidazoline based dithiocarbamate chain transfer agents (CTAs) were synthesized and utilized to control the polymerization of different less activated monomers. All CTAs other than imidazoline based ones were good to control the vinyl acetate polymerizations with respect to molecular weight of the polymer obtained and were reasonable with respect to the polydispersity index achieved. However the actual polydispersity of polymers depended on the reinitiating groups of the CTAs. The polymerizations of *N*-vinylpyrrolidone and vinyl benzoate were not well controlled by any of these CTAs. The kinetic study and chain extension reaction of vinyl acetate polymerizations proved that the polymerizations were pseudo-living in character and the ^{1}H NMR and UV-visible spectra of the resultant polymers confirmed the presence of dithiocarbamate end functionality. The good control in molecular weight and colorless nature of the resultant poly(vinyl acetate) may make these chain transfer agents interesting for applications where low polydispersity is not a very stringent requirement.

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Captions to figures and schemes

Figure 1. Different dithiocarbamate chain transfer agents (CTAs) synthesized and used in this study.

Figure 2. (i) ^{1}H NMR and (ii) ^{13}C NMR spectra of **CTA4**.

Figure 3. UV-visible spectra of different dithiocarbamate chain transfer agents **CTA1-5** in THF (concentration of CTA = 0.02 mg/ml).

Figure 4. (a) Kinetic plots and (b) evolution of molecular weight and polydispersity with conversion and (c) GPC traces of different polymer samples of the bulk polymerization of VAc using **CTA4** at 70 ^{o}C (VAc:**CTA4**:AIBN = 350:1:0.1).

Figure 5. GPC traces of PVAc and PVAc-*b*-PVBz copolymer obtained by chain extension reaction.

Figure 6. ^{1}HNMR spectra of (i) PVAc (**P20a**) and (ii) PVAc-*b*-PVBz copolymer (**P20b**) produced by chain extension reaction.

Figure 7. UV-visible spectra of **CTA4** (0.02 mg/ml) and different vinyl acetate (co)polymers in THF (Concentration: **P20a** (1 mg/ml), **P20b** (0.2 mg/ml) and **P1** (1 mg/ml)).

Figure 8. Photograph of (a) **CTA4**, (b) PVAc synthesized using **CTA4** (**P5**) and (c) PVAc-*b*-PVBz copolymer synthesized using **CTA4** (**P20b**).

Scheme 1. Synthesis of pyrrolidine and piperidine based CTAs.

Scheme 2. Synthesis of imidazoline based CTAs.

Scheme 3. Synthesis of vinyl acetate copolymers using **CTA4**.

Table 1. Bulk polymerization results of VAc using different dithiocarbamate CTAs.

Entry	Monomer	Chain transfer agent (CTA)	Time (h)	Conversion[b)] (%)	$M_{n,Theor}$	$M_{n,GPC}$[c)]	PDI [c)]
P1	VAc	None	1	56.7	NA	148700	2.97
P2	VAc	CTA1	27	36.4	3340	1360	1.71
P3	VAc	CTA2	19	89.9	8000	6030	1.60
P4	VAc	CTA3	4	85.5	7590	8200	1.51
P5	VAc	CTA4	7	78.6	6950	7330	1.48
P6[a)]	VAc	CTA4	16	91.3	27690	27530	1.46
P7	VAc	CTA5	7	81.2	7190	7240	1.46
P8	VAc	CTA6	24	45.1	4140	Oligomer	--
P9	VAc	CTA7	28	59.3	5350	Oligomer	--

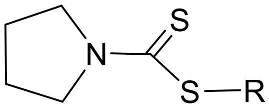
For all polymerization VAc:CTA:AIBN = 100:1:0.1; [a)]VAc:**CTA4**:AIBN = 350:1:0.1, in bulk and at 70 °C; [b)]determined by ^{1}H NMR analysis; [c)]in THF GPC using PS calibrations.

Table 2. RAFT polymerization results of other vinyl monomers using different dithiocarbamate CTAs.

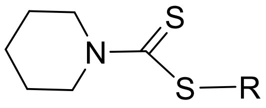
Entry	Monomer	Chain transfer agent (CTA)	Time (h)	Conversion[f] (%)	$M_{n,Theor}$	$M_{n,GPC}$[g]	PDI [g]
P10 [a]	MMA	CTA1	4	17	6160	55980	1.74
P11[a]	MMA	CTA1+pTSA[e]	4	17.3	6270	62680	1.70
P12[b]	St	CTA2	18	69.2	25210	74310	1.51
P13[b]	St	CTA2+TFMSA[e]	18	60.9	22470	59310	1.57
P14[c]	NVP	None	1	36.1	NA	116000	2.48
P15[c]	NVP	CTA1	24	10.9	2640	3010	1.60
P16[c]	NVP	CTA2	23	52.3	11890	13260	2.47
P17[c]	NVP	CTA3	3	44.2	10070	32730	2.08
P18[c]	NVP	CTA4	3	63.6	14320	28720	2.05
P19[d]	VBz	CTA4	24	20	6110	11490	1.75

[a] MMA:CTA:AIBN = 350:1:0.5; in toluene (74 volume %) and at 60 °C; [b] St:CTA:AIBN = 350:1:0.2; in bulk and at 80 °C; [c] Monomer:CTA:AIBN = 200:1:0.1, in bulk and at 60 °C; [d] VBz:CTA:AIBN = 200:1:0.1, in bulk and at 70 °C; [e] pTSA = *para*-toluenesulfonic acid and TFMSA = trifluoromethanesulfonic acid used were 2 times of the molar concentration of respective CTA used; [f] determined by ^{1}H NMR analysis; [g] PMMA, PS and PVBz were in THF GPC using PS calibrations and PNVP were in DMF GPC using PMMA calibrations.

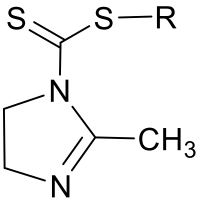
Figure 1. Different dithiocarbamate chain transfer agents (CTAs) synthesized and used in this study.



R = -$C(CH_3)_2CN$ **CTA1**
-$C(CH_3)_2CO_2Et$ **CTA2**
-$CH(CH_3)CO_2Me$ **CTA3**
-CH_2CN **CTA4**



R = -CH_2CN **CTA5**



R = -$CH(CH_3)CO_2Et$ **CTA6**
-CH_2CN **CTA7**

Figure 2. (i) ^{1}H NMR and (ii) ^{13}C NMR spectra of **CTA4**.

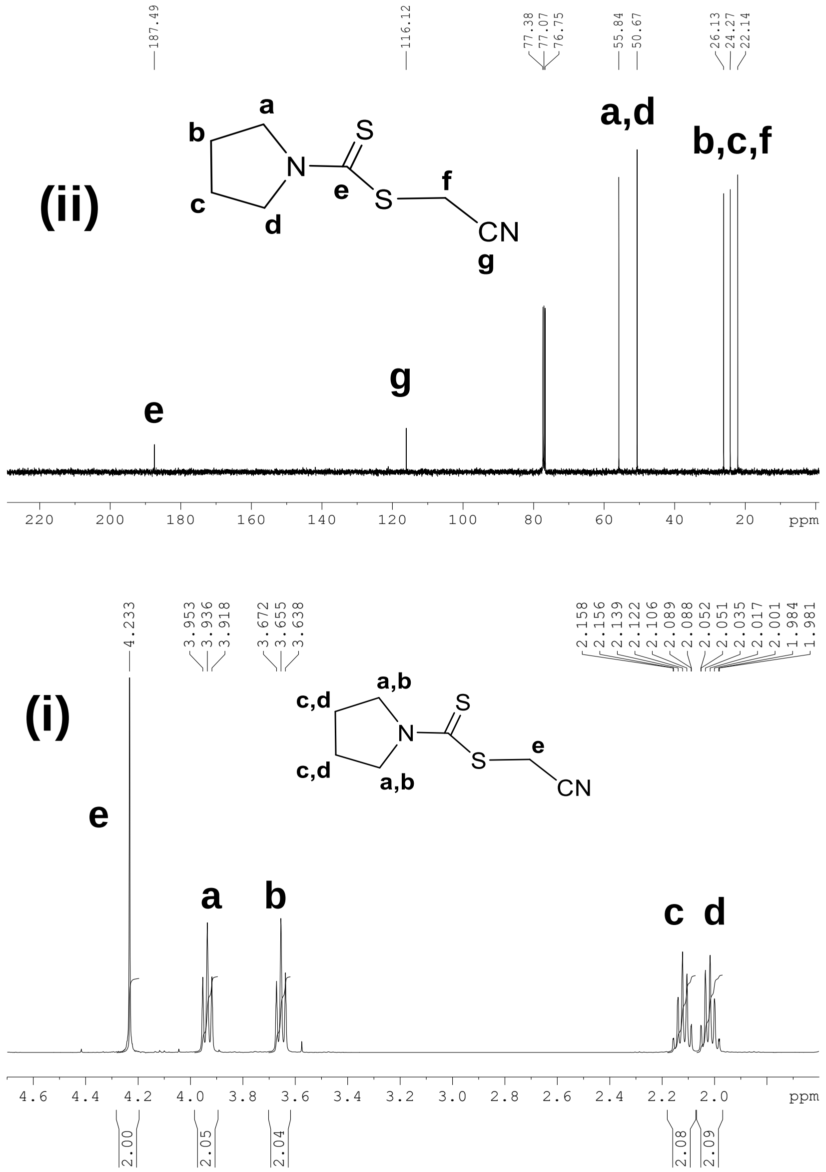


Figure 3. UV-visible spectra of different dithiocarbamate chain transfer agents **CTA1-5** in THF (concentration of CTA = 0.02 mg/ml).

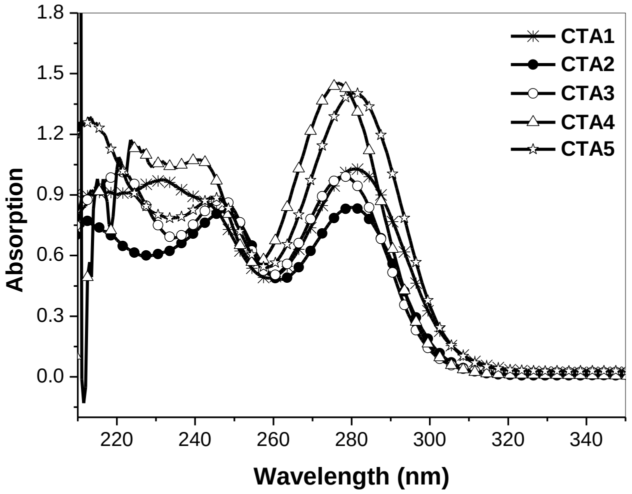


Figure 4. (a) Kinetic plots and (b) evolution of molecular weight and polydispersity with conversion and (c) GPC traces of different polymer samples of the bulk polymerization of VAc using **CTA4** at 70 °C (VAc:**CTA4**:AIBN = 350:1:0.1).

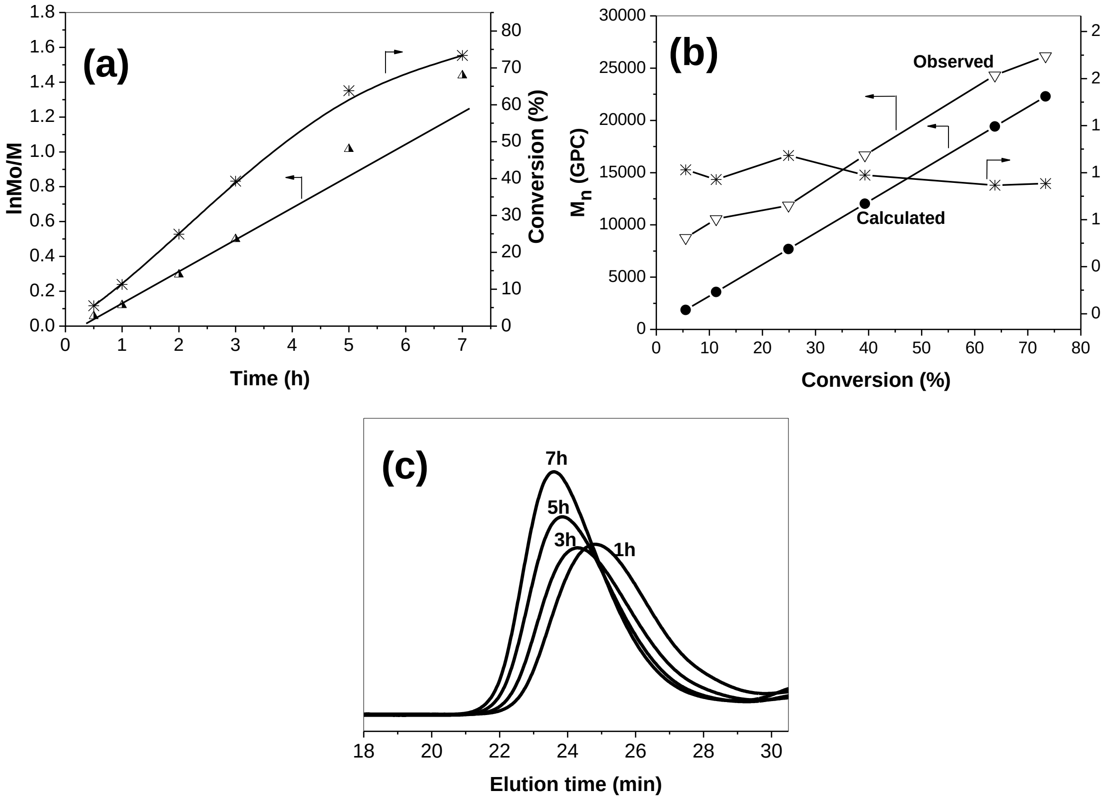


Figure 5. GPC traces of PVAc and PVAc-*b*-PVBz copolymer obtained by chain extension reaction.

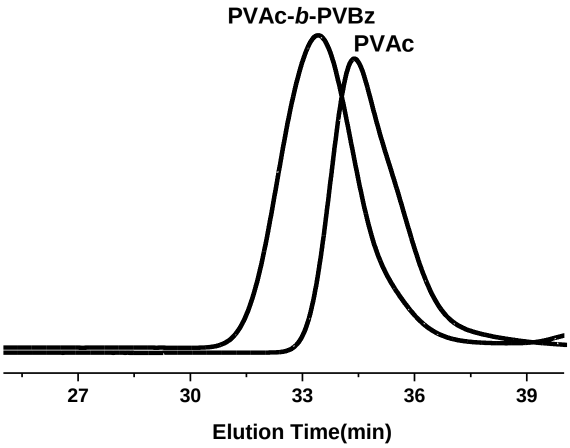


Figure 6. ^{1}HNMR spectra of (i) PVAc (**P20a**) and (ii) PVAc-*b*-PVBz copolymer (**P20b**) produced by chain extension reaction.

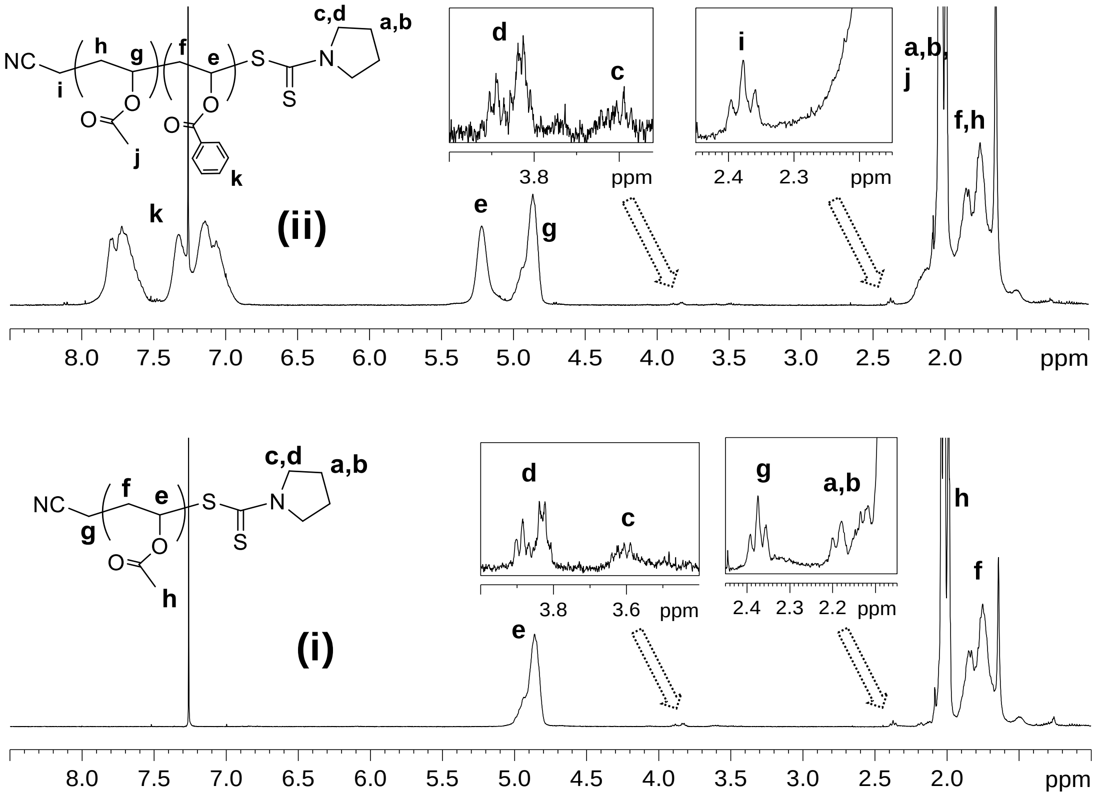
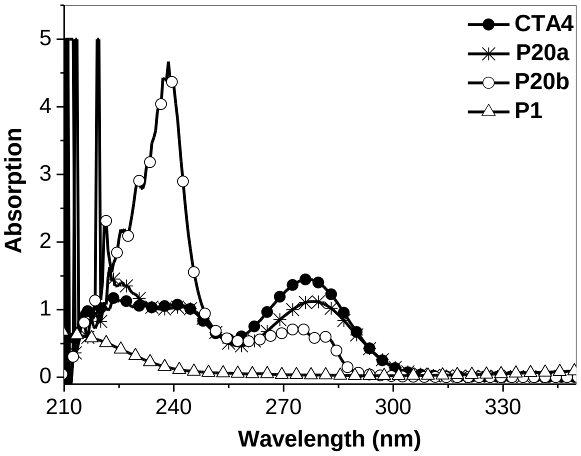


Figure 7. UV-visible spectra of **CTA4** (0.02 mg/ml) and different vinyl acetate (co)polymers in THF (Concentration: **P20a** (1 mg/ml), **P20b** (0.2 mg/ml) and **P1** (1 mg/ml)).



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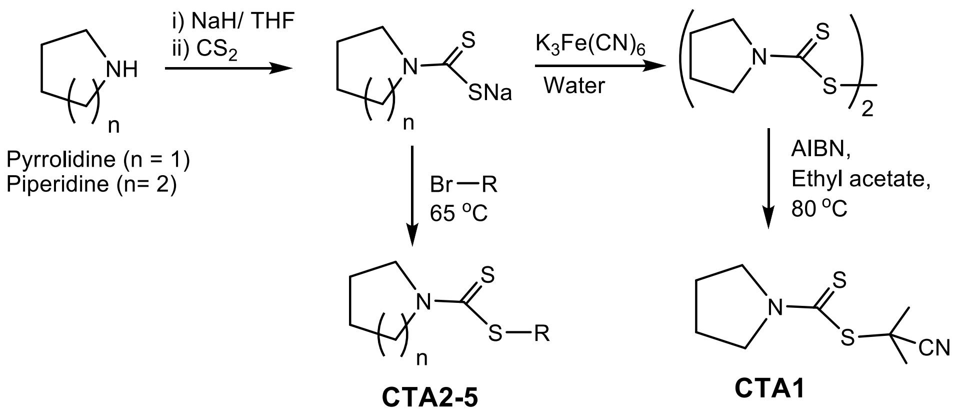
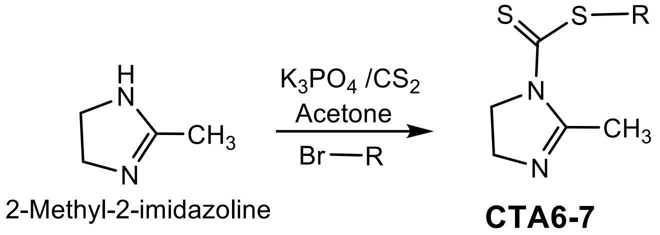
Scheme 1. Synthesis of pyrrolidine and piperidine based CTAs.



Scheme 2. Synthesis of imidazoline based CTAs.



Scheme 3. Synthesis of vinyl acetate copolymers using **CTA4**.

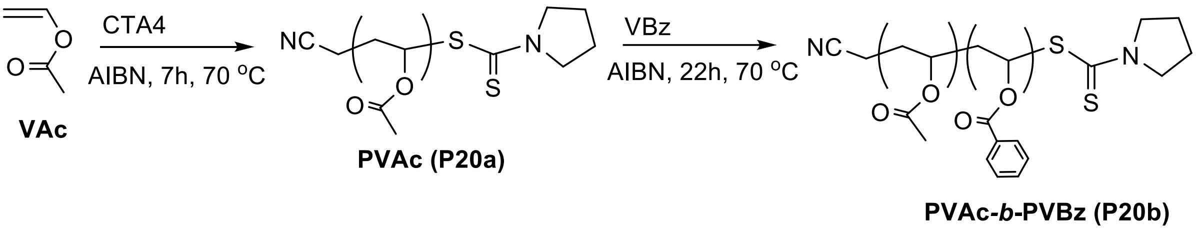


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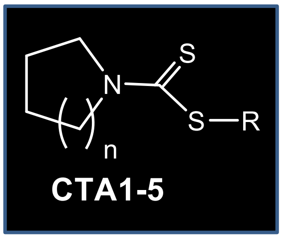
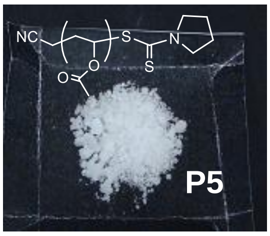
Table of contents

A series of cyclic amine based dithiocarbamate chain transfer agents (CTAs) were synthesized and utilized to control the polymerization of different less activated vinyl monomers. The effect of different activating and re-initiating groups of these dithiocarbamates towards polymerizations were investigated. The pyrrolidine and piperidine based CTAs were moderately good to control the vinyl acetate polymerization and produced almost colorless polymer when precipitated.





Authors: Satyasankar Jana,* Anbanandam Parthiban

Title: Cyclic Amine Based Dithiocarbamate Chain Transfer Agents for the RAFT Polymerization of Less Activated Monomers

Supporting information for

Macromolecular Chemistry and Physics

Cyclic Amine Based Dithiocarbamate Chain Transfer Agents for the RAFT Polymerization of Less Activated Monomers

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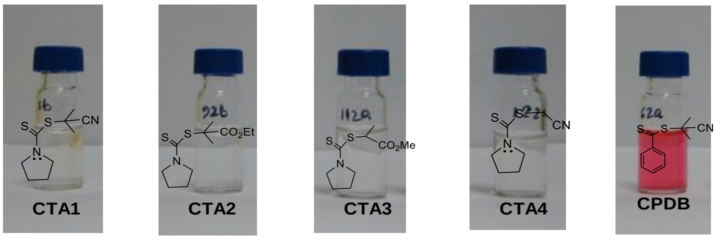

Figure S1. Photograph of the solutions of different dithiocarbamate chain transfer agents synthesized (**CTA1-4**) and 2-cyanoprop-2-yl dithiobenzoate (CPDB) (5 mg in 1.5 ml acetonitrile each).

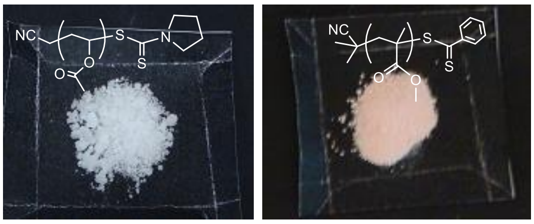

Figure S2. Photograph of (a) **P5** ($M_{n,GPC}$ ~ 7K, PDI ~1.5) and (b) PMMA ($M_{n,GPC}$ ~12k, PDI ~ 1.2) synthesized using 2-cyanoprop-2-yl dithiobenzoate.