(*S*)-2-(Ethyl propionate)-(*O*-ethyl xanthate) and (*S*)-2-(Ethyl isobutyrate)-(*O*-ethyl xanthate)-mediated RAFT polymerization of *N*-vinylpyrrolidone

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Abstract   (*S*)-2-(Ethyl propionate)-(*O*-ethyl xanthate) (X1) and the newly synthesized (*S*)-2-(ethyl isobutyrate)-(*O*-ethyl xanthate) (X2) were used as the reversible addition-fragmentation chain transfer (RAFT) agents for the radical polymerization of *N*-vinylpyrrolidone (NVP). The former showed the better chain transfer ability in the polymerization at 60 °C. Kinetics study with X1 shows the psuedo-first order kinetics upto 45% monomer conversion. Molecular weight (M_n) of the resulted polymer increases linearly with increase in the monomer conversion upto around 45%. Polydispersity of the corresponding poly(NVP)s increase gradually from 1.2 to 1.9 with increase in the monomer conversion. Chain-end analysis of the resulted polymer by ^{1}H NMR shows clearly that polymerization started with radical forming out of xanthate mediator. Living nature of the polymerization was confirmed from the successful homo chain extension experiment and also the hetero-chain extension experiment involving synthesis of poly(NVP)-b-polystyrene amphiphilic diblock copolymer.
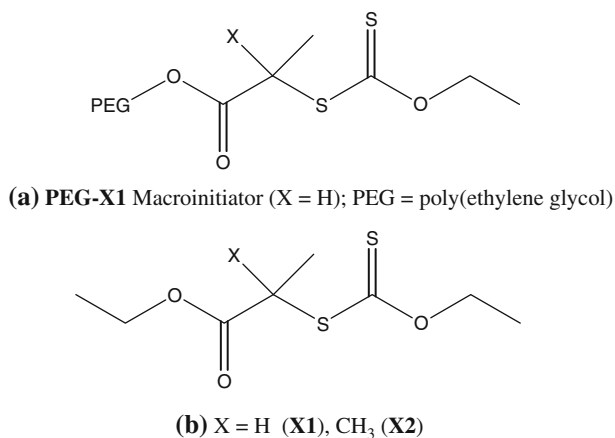
Keywords   Xanthate-mediated RAFT polymerization · *N*-vinylpyrrolidone ·
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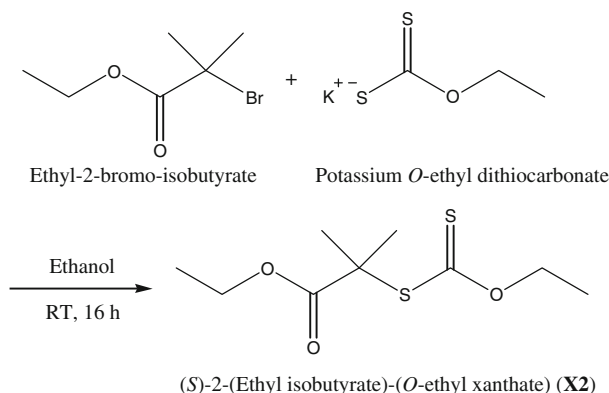
Introduction

Poly(*N*-vinylpyrrolidone) is used extensively in chemical and medical application due to its high water solubility, low toxicity, and biocompatibility. *N*-vinylpyrrolidone (NVP) can only be polymerized by radical polymerization due to the non-conjugation of its amidic keto group with the vinyl group. Different controlled/living radical polymerization methods [1–12] were explored for the controlled

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synthesis of its homopolymer and block-copolymer. Rizzardo et al. [1] reported first in a patent the reversible addition-fragmentation chain transfer (RAFT) polymerization of NVP. Later, Matyzaszewski et al. [2] reported the synthesis of low molecular weight (M_n = 2,000, PDI = 1.15) poly(NVP) using copper-catalyzed atom transfer radical polymerization (ATRP). In the both reports, the details were not disclosed. Using xanthate type RAFT agent, Kamigaito et al. [3] reported the controlled radical polymerization of NVP as well as the simultaneous control of molecular weight and tacticity of poly(NVP) by performing polymerization in fluoroalcohols. Gnanou et al. [4] also reported the controlled radical polymerization of NVP using dithiocarbamate-type RAFT agents. Hadjichristidis et al. [5] also reported the controlled radical polymerization of NVP using nitroxide-mediated and RAFT polymerization methods. Using organostibine [6, 7], organotellurium [8], and organobismuthine [9] mediators, Yamago et al. reported the synthesis of highly controlled PNVP homopolymers and its block copolymers. Recently, Lu et al. [10] reported the Cu-metal catalyzed ATRP of NVP using 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradecane(Me$_6$cyclam) as ligand in 1,4-dioxane/isopropanol mixture. Very recently, Klumperman et al. [11] studied extensively the mechanistic aspect of the xanthate-mediated RAFT polymerization of NVP. They also reported [12] the preliminary results on the homopolymerization of NVP using (S)-2-(ethyl propionate)-(O-ethyl xanthate) (X1) (Scheme 1) in presence of poly(ethylene glycol) monomethyl ether and also the synthesis of double hydrophilic blockcopolymer of poly(NVP) and poly(ethylene glycol) (PEG) starting with the xanthate X1 having a poly(ethylene glycol) (PEG) segment (PEG-X1 macroinitiator) (Scheme 1), but they did not report so far the detailed study of the RAFT polymerization of NVP using X1. Here, we have reported the synthesis of one new xanthate mediator (S)-2-(ethyl isobutyrate)-(O-ethyl xanthate) (X2) (Schemes 1, 2) and studied in detail the polymerization of NVP using these two xanthates (S)-2-(ethyl propionate)-(O-ethyl xanthate) (X1) and (S)-2-(ethyl isobutyrate)-(O-ethyl xanthate) (X2).

(a) **PEG-X1** Macroinitiator (X = H); PEG = poly(ethylene glycol)

(b) X = H (**X1**), CH$_3$ (**X2**)

Scheme 1

Ethyl-2-bromo-isobutyrate   Potassium *O*-ethyl dithiocarbonate

(*S*)-2-(Ethyl isobutyrate)-(*O*-ethyl xanthate) (**X2**)

Scheme 2

Experimental section

Materials

Ethyl-2-bromo-propionate (Aldrich, 99%), ethyl-2-bromo-isobutyrate (Aldrich, 98%), carbon disulfide (Loba Chemie, 95%), diethyl ether (s.d.fine), hexane (CDH), ethyl acetate (CDH), potassium hydroxide (Qualigens), anhydrous magnesium sulfate (Loba Chemie) were used as received. *N*-Vinylpyrrolidone (Aldrich, 99%) was dried over anhydrous magnesium sulfate and distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) (Spectrochem, 98%) was recrystallized from methanol. Ethanol (Saraya Distilliary, India) was left over CaO for overnight and distilled over fresh CaO. Synthesis of potassium *O*-ethyl xanthate [13] and (*S*)-2-(ethyl propionate)-(*O*-ethyl xanthate) (X1) was prepared according to the literature [12].

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL300 FTNMR (300 MHz) at ambient temperature in CDCl$_3$ or D$_2$O as solvent and are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak. The number average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by Younglin ACME 9000 Gel Permeation Chromatography in DMF at 40 °C with flow rate 1 ml/min on two polystyrene gel columns [PL gel 5 μm 10E 4 Å columns (300 × 7.5 mm)] connected in series to Younglin ACME 9000 Gradient Pump and a Younglin ACME 9000 RI detector. The columns were calibrated against seven poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10). The theoretical number average molecular weight [M_n(theor.)] was calculated using the following equation:

$$\overline{M}_n(\text{theor.}) = \frac{[\text{NVP}]_o}{[\text{X}]_o} \cdot X_{\text{NVP}} \cdot M_{\text{NVP}} + M_X$$

where X_{NVP} is the fraction conversion of monomer, M_{NVP} is the molecular weight of monomer, and M_X is the molecular weight of the xanthate mediator X.

Synthesis of potassium O-ethyl xanthate [13]

5.63 g (0.1 mol) KOH was stirred in 40 mL (0.645 mol) ethanol until a clear solution was obtained. Then, 20 mL (0.332 mol) CS_2 was added slowly to the above solution during stirring and the stirring was continued for overnight. The resulted mixture was suspended in 200 mL ether and filtered. The precipitate was washed thrice with ether and dried under vacuum at room temperature for overnight. Observed m.p. of the resulted light yellow color product was 210 °C.

Synthesis of (S)-2-(ethyl propionate)-(O-ethyl xanthate) (X1) [12]

9.50 g (58 mmol) potassium O-ethyl xanthate was added to a solution of 6.6 mL (9.48 g, 52.7 mmol) ethyl-2-bromo-propionate in 30 mL ethanol and stirred for 16 h at room temperature. The resulted white precipitate was filtered off. The filtrate was diluted with 250 mL diethyl ether and washed four times with 50 mL deionised water. Then the resulted diethyl ether solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to dryness. The yellow colored liquid product was purified by column chromatography using hexanes/ethyl acetate (95:5 v/v) as the eluent. A yellow-colored oily product (7.8 g, 67% yield) was obtained. ^{1}H NMR (300 MHz, CDCl$_3$): 4.63 (q, 2H, C(S)OCH_2), 4.37 (q, 1H, CH), 4.20 (q, 2H,C(O)OCH_2), 1.56 (d, 3H, CH_3CH), 1.41 (t, 3H, C(S) –OCH$_2$CH_3), 1.28 (t, 3H, C(O)OCH$_2$CH_3).^{13}C NMR (75 MHz, CDCl$_3$) :13.5, 13.9, 16.7, 47.0, 61.6, 70.0, 171.2, 211.9. Observed density of the product was 1.115 g/mL.

Synthesis of (S)-2-(ethyl isobutyrate)-(O-ethyl xanthate) (X2)

9.62 g (60 mmol) Potassium O-ethyl xanthate was added to a solution of 7.8 mL (10.28 g, 52.7 mmol) ethyl-2-bromo-isobutyrate in 35 mL ethanol and stirred for 16 h at room temperature. The resulted white precipitate was filtered off. The filtrate was diluted with 300 mL diethyl ether and washed four times with 50 mL deionised water. Then the resulted diethyl ether solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to dryness. The yellow-colored liquid product was purified by column chromatography using hexanes/ethyl acetate (95:5 v/v) as the eluent. A yellow-colored oily product (5.8 g, 47% yield) having severe pungent odor was obtained. ^{1}H NMR (300 MHz, CDCl$_3$): 4.63 (q, 2H, C(S)OCH_2), 4.20 (q, 2H,C(O)OCH_2), 1.56 (s, 6H, CH_3), 1.41 (t, 3H, C(S)OCH$_2$CH_3), 1.28 (t, 3H, C(O)OCH$_2$CH_3). ^{13}C NMR (300 MHz, CDCl$_3$): 13.2, 14.1, 24.6, 54.0, 61.5, 69.5, 172.8, 210.8. Observed density of the product was 1.12 g/mL.

Typical xanthate-mediated bulk polymerization of NVP

Definite amount of distilled NVP, recrystallized AIBN, and mediator X1/X2 were placed in a dry Schlenk tube and mixed thoroughly, and was purged with dry nitrogen gas for 30 min. The flask was immersed in an oil bath preheated at a desired temperature. After the definite time interval, reaction was stopped by dipping the Schlenk tube in liquid N_2. A small portion of the reaction mixture was taken out to determine the monomer conversion by ^{1}H NMR. The rest of the polymer mixture was dissolved in THF and precipitated from excess amount of hexane. The precipitated polymer was collected by centrifugation. The separated polymer was dried under vacuum at 50 °C for 12 h.

Polymerization procedure for the kinetic study

Typically, a mixture of 4 mL (4.16 g, 37.4 mmol) NVP, 24 μL (27.7 mg, 0.125 mmol) X1, and 4.1 mg (0.025 mmol) AIBN were placed in a dry Schlenk tube containing a teflon-coated magnetic bar and was purged with dry nitrogen gas for 30 min. This degassed stock solution was divided into seven dry and degassed polymerization glass tubes. The polymerization tubes were then placed in a thermostated bath at 60 °C for the desired time. The reaction was stopped by freezing the reaction mixture at liquid N_2 temperature. Monomer conversion (%) was determined using ^{1}H NMR by comparing the integrated peak area of the residual vinylic signals at 4.3–4.4 (2H) and 7.0–7.1 ppm (1H) of the monomer with that of the peak at 3.0–3.4 ppm (2H) of the corresponding polymer. The rest polymer mixture was dissolved in 2 mL THF and precipitated from 50 mL of hexane. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitated from hexane twice, and finally dried under vacuum at 50 °C for 12 h.

Synthesis of poly (NVP) macroinitiator (M_n = 3,800, PDI = 1.24)

Typically, a mixture of 2 mL (2.1 g, 18.7 mmol) NVP, 12 μL (13.9 mg, 0.06 mmol) X1, and 2 mg (0.01 mmol) AIBN were placed in a dry Schlenk tube containing a teflon-coated magnetic bar and was purged with dry nitrogen gas for 30 min. The polymerization tube was then placed in a thermostated bath at 60 °C for 3 h. The reaction was stopped by freezing the reaction mixture at liquid N_2 temperature. The reaction mixture was dissolved in 5 mL THF and precipitated from 100 mL hexane. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitated in hexane twice, and finally dried under vacuum at 50 °C for 12 h. Monomer conversion (15%) was gravimetrically determined. The molecular weight (M_n) and polydispersity index (PDI) (M_w/M_n) of the obtained polymer were observed at 3,800 and 1.24 respectively.

Self-blocking/homo-chain extension experiment

A mixture of 0.1 g (0.026 mmol) poly(NVP) macroinitiator (M_n = 3,800, PDI = 1.24), 0.9 mg (0.005 mmol) AIBN, and 84 µL (0.087 g, 0.786 mmol) NVP in 0.5 mL DMF was taken in a dry Schlenk tube containing a teflon-coated magnetic bar and was purged with dry nitrogen gas for 30 min. The polymerization tube was then placed in a thermostated bath at 80 °C for the 3 h. The reaction was stopped by freezing the reaction mixture at liquid N_2 temperature. The reaction mixture was dissolved in 2 mL THF and precipitated from 50 mL hexane. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitated in hexane twice, and finally was dried under vacuum at 50 °C for 12 h. Monomer conversion (44%) was gravimetrically determined. The molecular weight (M_n) and polydispersity index (PDI) (M_w/M_n) of the obtained polymer were observed at 5,600 and 1.51 respectively.

Synthesis of poly (*N*-vinyl pyrrolidone)-b-polystyrene

A mixture of 0.1 g (0.026 mmol) poly(NVP) macroinitiator (M_n = 3,800, PDI = 1.24), 0.9 mg (0.005 mmol) AIBN, and 90 µL (0.08 g, 0.786 mmol) Styrene in 0.5 mL DMF was taken in a dry Schlenk tube containing a teflon-coated magnetic bar and was purged with dry nitrogen gas for 30 min. The polymerization tube was then placed in a thermostated bath at 80 °C for the 12 h. The reaction was stopped by freezing the reaction mixture at liquid N_2 temperature. Monomer conversion (45%) was determined by ^{1}H NMR using a small portion of the reaction mixture. The rest polymer mixture was dissolved in 2 mL THF and precipitated from 50 mL hexane. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitated from diethyl ether thrice, and finally was dried under vacuum at 50 °C for 12 h. This block copolymer is soluble both in water and methanol which are solvent for PNVP homopolymers, but non-solvent for poystyrene homopolymers. So, this block copolymer contains poly(NVP) homopolymer as impurities. The molecular weight (M_n) and polydispersity index (PDI) (M_w/M_n) of the diethyl ether-precipitated polymer were observed at 5,200 and 1.26, respectively.

Results and discussion

In order to understand the suitability of the two xanthate mediators, X1 and X2, we have performed the bulk polymerization of NVP under different conditions. Polymerization conditions and the characterization data of all PNVP samples prepared are shown in Table 1. In run 1, bulk polymerization of NVP using X1 mediator was carried out by maintaining molar ratio [NVP]:[X1]:[AIBN] = 100:1:0.2 at 60 °C for 36 h. Monomer conversion was about 69%. Observed molecular weight (M_n) (6,000) was lower than the theoretical molecular weight (7,812), while the observed PDI was around 1.25. Under the same experimental conditions, polymerization of NVP using X2 mediator resulted in the formation of

Table 1 RAFT polymerization of NVP mediated with X1 and X2[a]

Run	NVP (equiv)	RAFT agent (equiv)	Temp (°C)	Time (h)	Conv (%)[b]	$M_{n(theor.)}^c$	$M_{n(GPC)}^d$	M_w/M_n^d
1	100	X1 (1)	60	36	69	7,812	6,000	1.25
2	100	X2 (1)	60	36	51	5,846	1,300	1.05
3	300	X1 (1)	60	28	45	15,086	10,300	1.90
4	300	X2 (1)	60	24	43	14,393	1,900	1.23
5	100	X1 (1)	80	2	80	9,022	5,800	1.80
6	100	X1 (1)	40	60	20	2,422	2,500	1.18
7	100	X2 (1)	80	17	53	6,130	1,500	1.39

[a] Bulk polymerization using 0.2 equivalent AIBN with respect to RAFT agent

[b] Determined by ^{1}H NMR

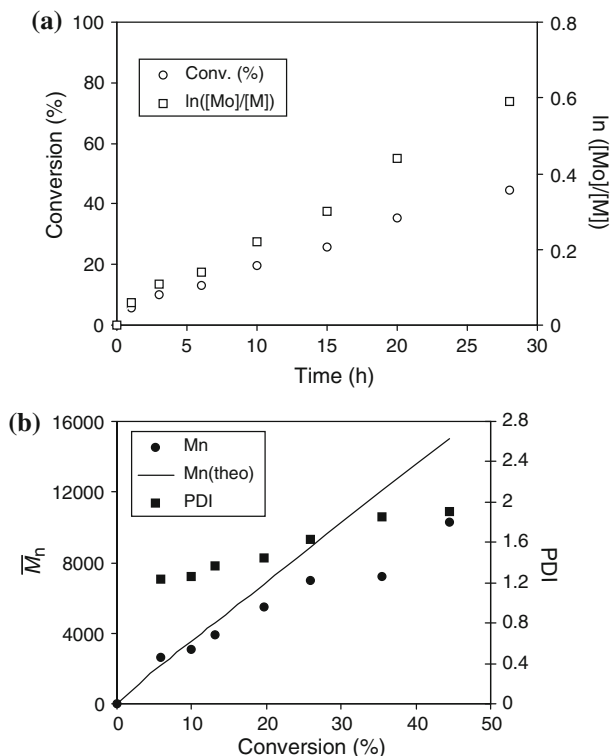[c] $\overline{M}_n(\text{theor.}) = \frac{[NVP]_o}{[X]_o} \cdot X_{NVP} \cdot M_{NVP} + M_X$

[d] Determined by GPC (DMF, 1 mL/min, 40 °C) calibrated against PMMA standard

oligomers (of molecular weight (M_n) around 1,300 with PDI around 1.05) at about 51% monomer conversion (run 2). Low polymer yields in both cases may be due to the side reactions involving NVP monomer itself and the loss of xanthate species from the polymer chain-end. Such type of results was reported in the xanthate-mediated polymerization of NVP [3, 14–16]. The formation of high molecular weight polymer with higher yield in case of X1 with respect to X2 can be explained considering the higher reactivity of less stable secondary carbon-centered radical derived from X1 mediator with respect to the lesser reactivity of the relatively stable tertiary carbon-centered radical derived from X2. The higher deviation of the molecular weight from the theoretical one even at higher monomer conversion in case of X2 may be due to (i) side reactions involving NVP monomer itself, (ii) side reactions involving the loss of the xanthate moieties from the chain-end, and (iii) very slow fragmentation of the oligomeric adduct from X2 than that from X1 under the experimental conditions [11, 14]. Similar types results in the xanthate-mediated polymerization are also reported in the literature [3, 14–16]. Formation of polymer with lower PDI using X2 may be due to the slower rate of the consumption of NVP monomer by the relatively stable tertiary carbon-centered radical derived from it than that by the relatively unstable secondary carbon-centered radical derived from X1. On further increase of monomer concentration from 100 equivalent to 300 equivalent keeping other conditions remained almost unchanged like run 1 and 2 (Table 1), the observed polymer yields were around 45% after 28 h for X1 mediator system (run 3) and 43% after 24 h for X2 mediator system (run 4). For run 3, the observed molecular weight (M_n) was about 10,300 with PDI around 1.90. This observed molecular weight was lower than the corresponding theoretical value (15,086). For run 4, the observed molecular weight (around 1,900 with PDI around 1.23.) was very much lower than the corresponding theoretical molecular weight (14,393). The increase in molecular weight is as expected from the higher monomer loading. But, the deviation of the observed M_n value from the corresponding theoretical values becomes higher with the increase of the monomer

loading. In addition, PDI of the resulted polymer also increases with the increase of the monomer loading. These results suggest the formation of the dead polymer due to the loss of the xanthate moieties from the chain-end or, chain transfer reaction to monomer. But, the insignificant increase in molecular weight even at considerable conversion (around 43%) in run 4 with X2 mediator is again confirming the formation of stable oligomeric xanthate adduct having very slow chain transfer constant apart from the occurrence of other side reactions [11]. While the temperature of the polymerization (using X1) increased to 80 °C (run 5) keeping other polymerization conditions like run 1, observed yield was around 80% after only 2 h. Faster polymerization with higher yield was observed due to higher temperature. The observed molecular weight of the resulted polymer was 5,800 with PDI around 1.80. Thus, this observed molecular weight value is close to that (6,000) observed for run 1. But the observed PDI is very much broader than that (1.25) observed with run 1. These results suggest the uncontrolled polymerization of NVP under such condition owing to the side reactions involving the formation of higher concentration of radical species. The polymerization at 40 °C (run 6) keeping other conditions remained unchanged like run 1 and run 5, the observed yield was only around 20% even after 60 h polymerization time. The observed molecular weight was 2,500 with PDI around 1.18. But the observed molecular weight was close to the corresponding theoretical value. Thus, the polymerization is more controlled at low temperature owing to the formation of low concentration of radical species and slow polymerization rate. On the other hand, polymerization of NVP using X2 at 80 °C keeping other conditions same like run 2 (run 7) results in the formation of oligomer having molecular weight 1,500 with PDI 1.39 at 53% monomer conversion after 17 h. So, the higher temperature also did not help in forming high molecular weight using X2 mediator, although there is a broadening of molecular weight distribution. This result is again confirming the above explanations for X2 mediator system as given against run 2 and run 4. Thus, the chain transfer ability of X1 mediator is better than X2 mediator in the bulk polymerization of NVP. Therefore, the bulk polymerization of NVP with molar ratio [NVP]:[X]:[AIBN] = 100:1:0.2 using X1 mediator gave best result in controlling molecular weight in the temperature range 40–60 °C.

In order to check the livingness of the polymerization system, the kinetic study of the bulk polymerization of NVP was carried out at 60 °C using X1 mediator with molar ratio [NVP]:[X1]:[AIBN] = 300:1:0.2. Figure 1a shows the plot of the monomer conversion (%) and $\ln([M_o]/[M])$ versus time. Monomer conversion (%) increases almost linearly upto around 45% conversion. The corresponding plot of $\ln([M_o]/[M])$ versus time is linear upto around 45% conversion. So the pseudo-first order monomer conversion rate was followed upto around 45% conversion. Figure 1b shows the plot of M_n and PDI versus monomer conversion (%). Molecular weight increases linearly with conversion (%) upto around 45%. But the observed molecular weights drifted gradually from the corresponding theoretical values with increase in conversion. The corresponding PDI increases gradually from 1.24 to 1.90 with increase in conversion. Figure 2 shows the corresponding gradual peak shifting of the GPC chromatograms in the above-mentioned kinetic study. All these results indicate that the propagating radical species concentration decreases slowly
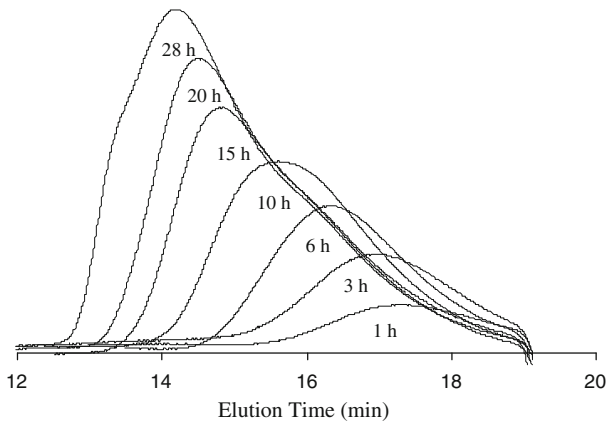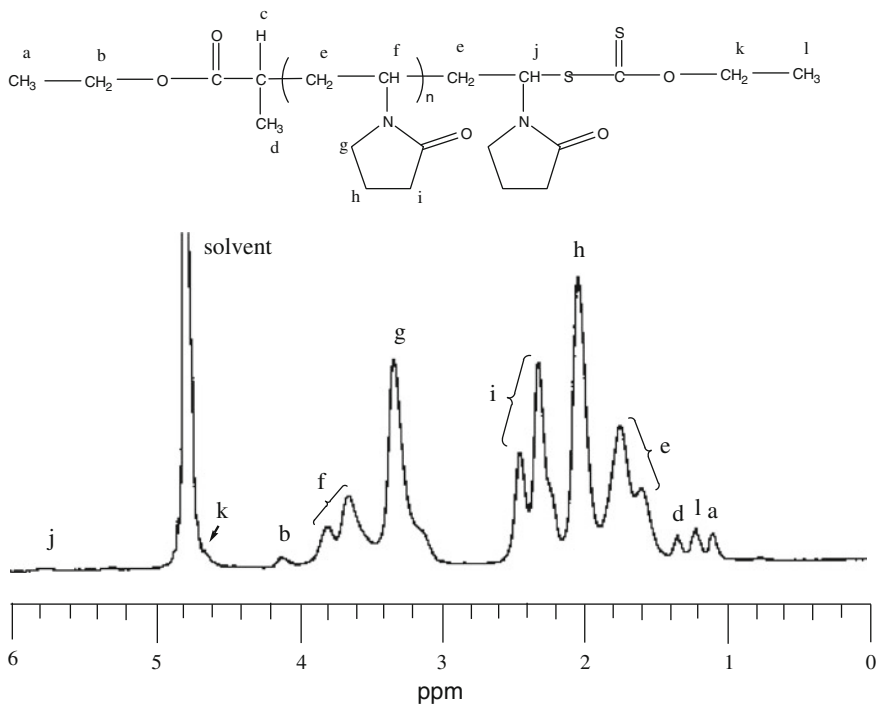
Fig. 1 **a** Plots of time versus monomer conversion and $\ln[M_o]/[M]$ (where $[M_o]$ = concentration of the monomer at time t = 0 min and $[M]$ = concentration of the monomer at the corresponding time) and **b** Plots of number-average molecular weight M_n and polydispersity (PDI) versus monomer conversion in the bulk polymerization of N-vinylpyrrolidone using [NVP] = 37.4 mmol, [X1] = 0.125 mmol, and [AIBN] = 0.025 mmol at 60 °C

with increase in conversion. It may be either due to the loss of xanthate moieties from the chain-end or, due to the considerable chain transfer reaction to monomer.

Figure 3 shows the end-group analysis of poly(NVP) sample, having M_n (GPC) = 3,200 with PDI = 1.34 obtained by the bulk polymerization of NVP using [NVP]:[X1]:[AIBN] = 300:1:0.2 at 60 °C for 3 h, by ^{1}H NMR (300 MHz) spectroscopy in D_2O solvent. Peaks from e to j are the characteristic repeating unit of the NVP as assigned in the figure. Rest peaks are coming from the X1 mediator. All 2-(ethyl propionate) protons except methine proton c are observed at around 1.1, 4.12, and 1.37 ppm, respectively. Methine proton c of 2-ethyl propionate is overlapped in the peak of the methylene protons i adjacent to the keto group of the repeating unit. We also did not able to find a separate peak of methine proton c using $CDCl_3$ and DMSO-d_6 solvents. In addition, O-ethyl protons are observed at 1.24 and 4.6 ppm, respectively. The peak of the methine proton j of the terminal NVP group close to O-ethylxanthate group is observed at around 5.6 ppm. The number average degree of polymerization for this polymer is calculated by dividing the total peak area of (f + g) by the peak area of a or l.

Fig. 2 Gradual shifting of the gel permeation chromatograms in the kinetic study of the bulk polymerization of *N*-vinylpyrrolidone using [NVP] = 37.4 mmol, [X1] = 0.125 mmol and [AIBN] = 0.025 mmol

Fig. 3 ^{1}H spectrum of (300 MHz, D$_2$O) of poly(*N*-vinylpyrrolidone) prepared in the bulk polymerization of *N*-vinylpyrrolidone using [NVP] = 18.7 mmol, [X1] = 0.06 mmol and [AIBN] = 0.01 mmol at 60 °C for 3 h

Table 2 Chain-extension experiment[a]

Run	Monomer (equiv.)	Macroinitiator[b] ($\overline{M}_n$/PDI) (equiv.)	Time (h)	Yield (%)[c] (Grav.)	Conv % (NMR)[d]	M_n (theor.)[e]	$\overline{M}_n$/PDI (GPC)[f]	X_{PNVP} (NMR)[g]	X_{PNVP} (GPC)[g]
1	NVP (30)	(3,800/1.24) (1)	3	44	–	5,267	5,600/ 1.51	–	–
2	Styrene (30)	(3,800/1.24) (1)	12	–	45	5,204	5,200/ 1.26	0.93	0.73

[a] Using 0.2 equivalent AIBN in 0.5 mL DMF at 80 °C

[b] Macroinitiator used was PNVP-X1

[c] Conversion was determined gravimetrically

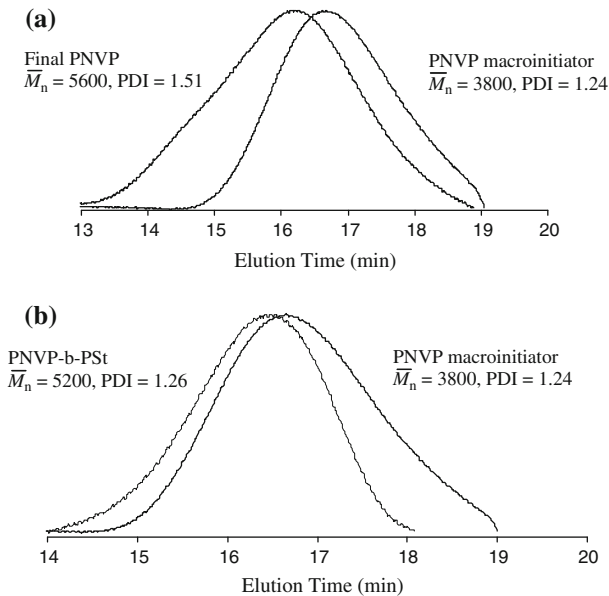[d] Conversion was determined by ^{1}H NMR

[e] M_n(theor.) = molecular weight of poly(NVP) + ([styrene]$_o$/[poly(NVP)]$_o$ × fraction conversion of styrene × molecular weight of styrene)

[f] Determined by GPC(DMF, 1 mL/min, 40 °C) calibrated against PMMA standard

[g] X_{PNVP} = mol-fraction of PNVP

The corresponding M_n (NMR)s were 3,243 or 3,127, respectively, which are close to the value (3200) obtained by GPC measurement calibrated against poly(methyl methacrylate) standards. This indicates the formation of single chain from one molecule of xanthate mediator.

Table 2 shows the results of the homo and hetero chain extension experiments. Molecular weight and PDI of the poly(NVP) macro-initiator used for these experiments are 3,800 and 1.24 respectively. Homo-chain-extension experiment was performed in DMF using [NVP]: [macro-initiator]: [AIBN] = 30:1:0.2 at 80 °C for 3 h with 44% monomer conversion. Resulted polymer was precipitated from excess hexane and dried. The observed molecular weight and PDI of the resulted polymer was 5,600 and 1.51, respectively. This experimental (GPC) molecular weight [M_n(GPC) = 5,600] is closer to the corresponding theoretical one [M_n(theor.) = 5,204] (Table 2). The corresponding GPC chromatograms for homo-chain extension experiment (Fig. 4a) clearly show the shifting of the GPC chromatograms towards high molecular weight. This experiment is confirming the existence of active xanthate group at the chain-end of the macro-initiator. This is also supported from the successful synthesis of poly(NVP)-b-polystyrene starting from the same poly(NVP) macro-initiator. Block copolymerization was carried out in DMF using [St]:[poly(NVP) macro-initiator]:[AIBN] = 30:1:0.2 at 80 °C for 12 h with 45% monomer conversion. Resulted polymer was purified by repeated dissolution in tetrahydrofuran and precipitation from diethyl ether, which is solvent for polystyrene, but non-solvent for poly(NVP). This block copolymer is soluble both in water and methanol, which are solvent for PNVP homopolymer, but non-solvent for poystyrene homopolymer. So, this block copolymer may contain poly(NVP) homopolymer as impurities. The observed experimental (GPC) molecular weight (M_n) and PDI of this block copolymer was 5,200 and 1.26, respectively. The experimental (GPC) molecular weight is also close to the theoretical one [M_n(theor.) = 5,204] (Table 2). Figure 4b shows the corresponding GPC chromatograms for the hetero-chain
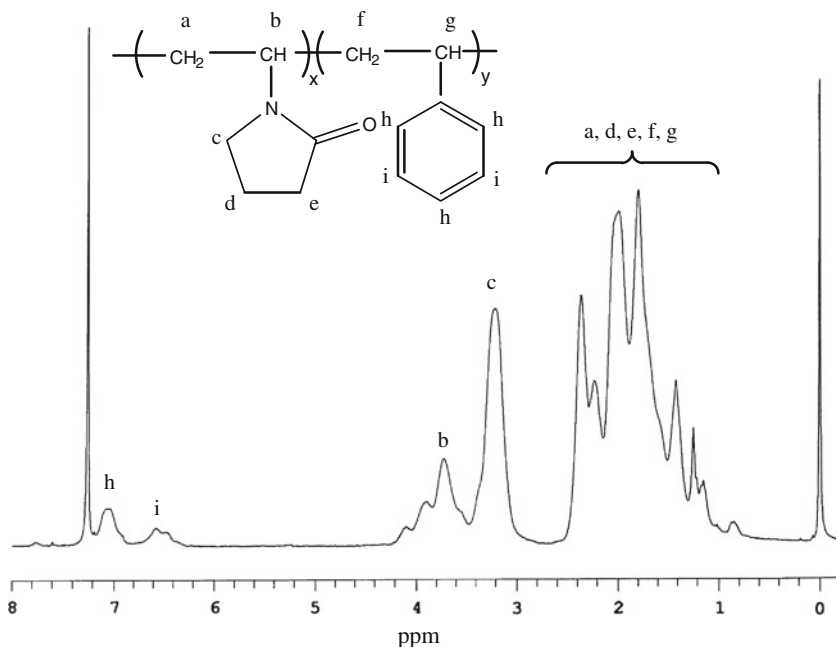
Fig. 4 a Gel permeation chromatograms of poly(N-vinylpyrrolidone) macroinitiator and final poly(N-vinylpyrrolidone) in the homo-chain extension experiment. b Gel permeation chromatograms of poly(N-vinylpyrrolidone) macroinitiator and the resulted poly(N-vinylpyrrolidone)-b-polystyrene in the hetero-chain extension experiment

extension experiments. It is clearly showing the shifting of the GPC chromatograms towards high molecular weight. High solubility of this block copolymer in water and methanol is due to the relatively shorter polystyrene segment ($M_n = 1,400$) with respect to that of longer PNVP segment ($M_n = 3800$). Moreover, the ^{1}H NMR of this block copolymer (Fig. 5) in CDCl$_3$ solvent shows clearly, in addition to the characteristic peaks of the poly(NVP) block, the presence of the peaks of the aromatic protons at around 6.6 and 7.1 ppm apart from that of the backbone chain methylene and methine protons of polystyrene block in the overlapped zone of 1.2–2.3 ppm. This is confirming the formation of the block copolymer of NVP and styrene. The observed mole fractions of poly(NVP) block in this block copolymer were 0.73 calculated on the basis of GPC molecular weights of the block copolymer and poly(NVP) macroinitiator and 0.93 calculated on the basis of ^{1}H NMR of this block copolymer (Table 2). So, the higher value of poly(NVP) fraction in the block copolymer from ^{1}H NMR measurement supports the presence of poly(NVP) homopolymer as impurities. Therefore, the successful occurrence of these chain extension experiments support the living nature of the NVP polymerization using X1 mediator.

Conclusion

Thus, (S)-2-(ethyl propionate)-(O-ethyl xanthate) (X1) and the newly synthesized (S)-2-(ethyl isobutyrate)-(O-ethyl xanthate) (X2) were used as the RAFT chain

Fig. 5 ^{1}H spectrum of (300 MHz, CDCl$_3$) of poly(*N*-vinylpyrrolidone)-b-polystyrene

transfer agents for the radical polymerization of NVP. The former showed the better chain transfer ability in the polymerization at 60 °C. Kinetics study with X1 shows the psuedo-first order kinetics upto 45% monomer conversion. Molecular weight (M_n) of the resulted polymer increases linearly with increase in the monomer conversion upto around 45%. Polydispersity of the corresponding poly(NVP)s increase gradually from 1.2 to 1.9 with increase in the monomer conversion. Chain-end analysis of the resulted polymer by ^{1}H NMR shows clearly that polymerization started with radical forming out of xanthate mediator. Living nature of the polymerization was confirmed from the successful homo chain extension experiment and also the hetero-chain extension experiment involving synthesis of poly(NVP)-b-polystyrene amphiphilic diblock copolymer.

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