

(S)-2-(Ethyl propionate)-(O-ethyl xanthate)- and (S)-2-(Ethyl isobutyrate)-(O-ethyl xanthate)-Mediated RAFT Polymerization of Vinyl Acetate

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ABSTRACT: (S)-2-(Ethyl propionate)-(O-ethyl xanthate) (X1) and (S)-2-(Ethyl isobutyrate)-(O-ethyl xanthate) (X2) were used as the reversible addition-fragmentation chain transfer (RAFT) agents for the radical polymerization of vinyl acetate (VAc). The former showed the better chain transfer ability in the polymerization at 60°C. Kinetic study with both RAFT agents showed pseudo-first order kinetics up to around 85% monomer conversion. Molecular weight of the resulting polymer increased linearly with increase in the monomer conversion up to around 85%. The observed molecular weights calculated from ¹H-NMR spectrum [M_n (NMR)] are close to the corresponding theoretical molecular weights [M_n (theor)]. The corresponding polydispersity index (PDI) of the resulting polymers

remained almost constant at around 1.2 up to ~ 65% monomer conversion and then increased gradually with the further increase in the monomer conversion. Chain-end analysis of the resulting polymers by ¹H-NMR showed clearly that polymerization started with the radical forming out of the xanthate mediator. The negligible homo-chain extension and the hetero-chain extension involving synthesis of poly(VAc)-*b*-poly(NVP) diblock copolymer were occurred. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2946–2955, 2012

Key words: (S)-2-(ethyl propionate)-(O-ethyl xanthate); (S)-2-(ethyl isobutyrate)-(O-ethyl xanthate); vinyl acetate; RAFT polymerization; kinetics

INTRODUCTION

Poly(vinyl acetate) (PVAc) was used extensively in industries like adhesives, paints, and pharmaceutical^{1–3}; hence, the controlled polymerization of vinyl acetate (VAc) will be desirable for specific applications. Polymerization of VAc proceeds only through a radical mechanism owing to the presence of an unconjugated electron donating acetate group [—O—C(=O)CH₃]. Chain-transfer and chain-termination reactions are well known in its radical polymerization process. So, it is a challenge to control its radical polymerization. The following controlled radical polymerization techniques^{4–24} were explored for the polymerization of VAc: degenerative transfer (DT) polymerization with alkyl iodides,^{4,5} reversible

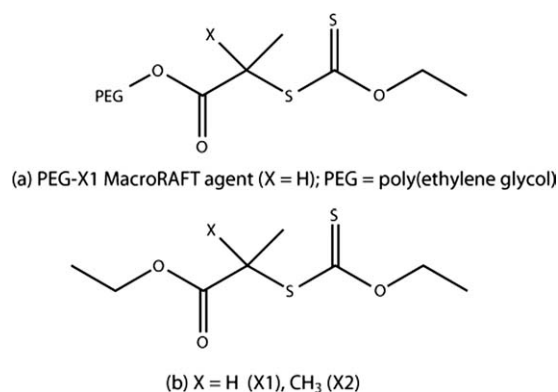
addition-fragmentation chain transfer (RAFT) polymerization mediated by xanthate^{6–17} and dithiocarbamates,^{18–20} organotellurium-mediated²¹ and organostibine-mediated²² chain transfer polymerization, iron-catalyzed^{23,24} atom transfer radical polymerization, and cobalt-mediated^{25–28} radical polymerization. Among these, xanthate-mediated RAFT polymerization was studied most. Stenzel et al.⁷ first used the xanthate as the chain transfer agent for RAFT polymerization of VAc and showed the influence of RAFT/MADIX (macromolecular design via the interchange of xanthates) agent's structure on its polymerization. They showed that the ethoxy Z-group retards with the slowest rate and the R-group should be a good leaving group and have a comparable reactivity towards the monomer like the growing macroradicals. Coote and Radom⁸ reported the *ab initio* calculations for the substituents effect in xanthate-mediated polymerization of VAc. Stenzel et al.⁹ also reported the FT/NIR and ¹H-NMR spectroscopic studies on the factors affecting the inhibition in the xanthate-mediated polymerization of VAc. Simms et al.¹⁰ reported the successful implementation of the xanthate-mediated polymerization of VAc in a miniemulsion process. Stenzel et al.¹¹ also reported the synthesis of poly(vinyl ester) (PVAc) star polymers via xanthate-mediated RAFT polymerization. Using the same method, they¹² also

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Scheme 1 Structure of RAFT agents.

reported the synthesis of poly(vinyl alcohol) combs. Recently, Klumperman et al.¹³ reported the synthesis of block copolymer of PVAc and poly(ethylene glycol) (PEG) starting with the xanthate X1 having a poly(ethylene glycol) (PEG) segment (PEG-X1 macroRAFT agent) [Scheme 1(a)]. Li et al.¹⁴ also recently reported the synthesis of two di-functional compounds containing an activated halide group and a xanthate group namely *S*-(2-chloropropionyethoxycarbonylmethyl) *O*-ethyl xanthate and *S*-(2-bromo-2-methylpropionyethoxycarbonylmethyl) *O*-ethyl xanthate and used successfully the same for the synthesis of well-defined poly(vinyl acetate)-*b*-polystyrene by combination of halide-mediated ATRP of styrene and xanthate-mediated RAFT polymerization of VAc. Very recently, Mahanthappa et al.¹⁵ reported the homopolymerization and block copolymerization of vinyl acetate, vinyl pivalate, and vinyl benzoate using (*S*)-2-(ethyl propionate)-(*O*-ethyl xanthate) (X1) as RAFT agent. [Scheme 1(b)]. Without mentioning the polymerization time, they only reported the results of the kinetic study of the controlled polymerization of VAc up to 40% monomer conversion using [X1] : [AIBN] = 10 : 1. Here, we report the detailed study of the polymerization of VAc using X1 at [X1] : [AIBN] = 5 : 1. Moreover, to study the effect of the structure of the leaving group in X1 xanthate containing ethoxy Z-group, we also report here the polymerization of VAc using one new xanthate mediator (*S*)-2-(ethyl isobutyrate)-(*O*-ethyl xanthate) (X2) recently reported by us [Scheme 1(b)].²⁹

EXPERIMENTAL

Materials

Ethyl-2-bromo-propionate (99%, Aldrich, Steinheim, Germany), ethyl-2-bromo-isobutyrate (98%, Aldrich, Steinheim, Germany), carbon disulfide (95%, Loba Chemie, Mumbai, India), diethyl ether (s.d.fine, Mumbai, India), hexane (CDH, Mumbai, India), ethyl acetate (CDH, Mumbai, India), potassium hy-

droxide (Qualigens, Mumbai, India), and anhydrous magnesium sulfate (Loba Chemie, Mumbai, India) were used as received. Vinyl acetate (Loba Chemie, Mumbai, India) was dried over anhydrous magnesium sulfate and distilled under reduced pressure. 2, 2'-Azobis(isobutyronitrile) (AIBN) (98%, Spectrochem, Mumbai, India) was recrystallized from methanol. Ethanol (Saraya Distilliary, India) was stirred over CaO overnight and distilled over fresh CaO. DMF (Loba Chemie, Mumbai, India) was purified first by the distillation of the azeotropic mixture of water and benzene and then distillation over anhydrous MgSO₄. Potassium *O*-ethyl xanthate, (*S*)-2-(Ethyl propionate)-(*O*-ethyl xanthate) (X1), and (*S*)-2-(Ethyl isobutyrate)-(*O*-ethyl xanthate) (X2) were prepared according to our previous work.²⁹

Measurements

¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL AL300 FTNMR (300 MHz) at ambient temperature in CDCl₃ as solvent and are reported in parts per million (δ) from internal tetramethylsilane or residual solvent peak. VAc monomer conversion (%) was calculated using ¹H-NMR spectroscopy in CDCl₃ by comparing the integrated peak area of the 1H of vinylic CH₂ proton of the monomer at 4.6 ppm with the combined peak area of 1H of another vinylic CH₂ proton of the monomer and 1H of backbone methine (CH) proton of the corresponding polymer at 4.9 ppm. The number average molecular weight of the polymer from its ¹H-NMR [*M_n*(NMR)] was calculated by comparing the peak area of the backbone methine proton of the polymer at 4.86 ppm with that of the methylene protons of the α-chain-end of the polymer at 4.6 ppm. The number average molecular weight [*M_n*(GPC)] and polydispersity index (*M_w*/*M_n*) (PDI) 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 mm²)] 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*(theo.)] was calculated using the following equation:

$$\bar{M}_n(\text{theor}) = \frac{[\text{VAc}]}{[\text{X}]_0} \cdot x_{\text{VAc}} \cdot M_{\text{VAc}} + M_X$$

where, *x*_{VAc} is the fraction conversion of monomer, *M*_{VAc} is the molecular weight of monomer and *M*_X is the molecular weight of the xanthate mediator X.

Synthesis of potassium *O*-ethyl xanthate

Totally, 5.63 g (0.1 mol) KOH was stirred in 40 mL (0.645 mol) ethanol until a clear solution was obtained.²⁹ Then, 20 mL (0.332 mol) CS₂ 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 overnight. Observed m.p. of the light yellow color product was 210°C.

Synthesis of (S)-2-(Ethyl propionate)-(O-ethyl xanthate) (X1)

Totally, 9.50 g (58 mmol) potassium *O*-ethyl xanthate²⁹ 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 resultant white precipitate was filtered off. The filtrate was diluted with 250 mL diethyl ether and washed four times with 50 mL deionized water, dried over anhydrous magnesium sulfate, filtered, and 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. ¹H-NMR (300 MHz, CDCl₃): 4.63 (q, 2H, C(O)OCH₂), 4.37 (q, 1H, CH), 4.20 (q, 2H, C(S)OCH₂), 1.56 (d, 3H, CH₃CH), 1.41 (t, 3H, C(O)-OCH₂CH₃), 1.28 (t, 3H, C(S)-OCH₂-CH₃). ¹³C-NMR (75 MHz, CDCl₃): 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)

Totally, 9.62 g (60 mmol) potassium *O*-ethyl xanthate²⁹ 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 resultant white precipitate was filtered off and purified as described for X1 in the previous section. Finally, a yellow colored oily product (5.8 g, 47% yield) having severe pungent odor was obtained. ¹H-NMR (300 MHz, CDCl₃): 4.63 (q, 2H, C(O)OCH₂), 4.20 (q, 2H, C(S)OCH₂), 1.56 (s, 6H, CH₃), 1.41 (t, 3H, C(O)-OCH₂CH₃), 1.28 (t, 3H, C(S)-OCH₂CH₃). ¹³C-NMR (300 MHz, CDCl₃): 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 VAc

Definite amount of recrystallized AIBN was placed in a dry Schlenk tube containing a Teflon-coated

magnetic bar, and then repeatedly degassed-and-filled with dry nitrogen thrice. To it, the definite amounts of already nitrogen purged VAc and the required xanthate (X1/X2) were added during nitrogen purging, and mixed thoroughly. The flask was immersed in an oil bath preheated at a desired temperature. After the definite time interval, the reaction was stopped by dipping the Schlenk tube in liquid N₂. A small portion of the polymerization mixture was used to determine the monomer conversion by ¹H-NMR. From the remaining part of the polymerization mixture, the resulting polymer was recovered by the evaporation of the monomer under reduced pressure.

Polymerization procedure for the kinetic study

Typically, 11.9 mg (0.072 mmol) recrystallized AIBN was placed in a dry Schlenk tube containing a teflon coated magnetic bar, and then repeatedly degassed-and-filled with dry nitrogen thrice. To it, 5 mL (4.67 g, 54.2 mmol) VAc, and 70 μL (80.1 mg, 0.36 mmol) X1, both of which were already purged with nitrogen, were added, and mixed thoroughly. The above stock solution was divided into six dry and degassed polymerization glass tubes fitted with a rubber septum. The polymerization tubes were then placed in a thermostated bath at 60°C. The reaction was stopped by freezing the reaction mixture with liquid N₂ at the desired time. Monomer conversion (%) was determined by ¹H-NMR. The resulted polymer was recovered by the evaporation of monomer under reduced pressure. Similar procedure was followed for the kinetic study using X2 as xanthate mediator with the recipe: 6 mL (5.6 g, 65.1 mmol) VAc, 91.5 μL (102.4 mg, 0.43 mmol) X2, and 14.3 mg (0.087 mmol) AIBN.

Synthesis of VAc macroRAFT agent using X1 (PVAc-X1)

In a dry Schlenk tube containing a teflon-coated magnetic bar, 11.9 mg (0.072 mmol) recrystallized AIBN was placed, and then repeatedly degassed-and-filled with dry nitrogen thrice. To it, 5 mL (4.67 g, 54.2 mmol) VAc and 70 μL (80.1 mg, 0.36 mmol) X1, both of which were already purged with nitrogen, were added during nitrogen purging, and mixed thoroughly. The polymerization tube was then placed in a thermostated bath at 60°C for 30 min. The reaction was stopped by cooling with liquid N₂. Monomer conversion (11.5%) was determined by ¹H-NMR using a small part of the reaction mixture. The remaining part of the polymerization mixture was dissolved in 8 mL THF, and precipitated from 200 mL of hexanes. The precipitated polymer was collected by centrifugation. The

TABLE 1
RAFT Polymerization of VAc Mediated with X1 and X2^a

Run	VAc (equiv)	Xanthate (equiv)	Time (h)	Temp. (°C)	Conv(%) NMR ^b	M_n (Theor) ^c	M_n (NMR) ^d	M_n (GPC) ^e	M_w/M_n ^e
1	100	X1(1)	3	60	87	7700	7400	13,500	1.30
2	100	X2(1)	4	60	67	6200	6100	13,600	1.35
3	150	X1(1)	3	60	86	11,300	10,000	18,900	1.33
4	150	X2(1)	4	60	84	11,100	9500	18,500	1.38
5	300	X1(1)	4	60	89	23,100	19,300	40,600	1.44
6	300	X2(1)	5	60	80	20,800	17,200	44,200	1.68
7	700	X1(1)	15	60	86	51,700	34,000	86,100	1.78
8	100	X1(1)	36	40	70	6200	4700	10,800	1.18
9	100	X1(1)	9	50	87	7700	5900	11,400	1.25

^a Bulk polymerization using 0.2 equiv AIBN with respect to RAFT agent.

^b Determined by ¹H-NMR.

^c $\bar{M}_n(\text{theor}) = \frac{[\text{VAc}]_0}{[\text{X}]_0} \cdot x_{\text{VAc}} \cdot M_{\text{VAc}} + M_{\text{X}}$.

^d $\bar{M}_n(\text{NMR}) = \frac{2 \times \text{peak area of backbone} - \text{CH proton at 4.86 ppm}}{\text{peak area of } -\text{CH}_2 \text{ proton of the } \alpha - \text{chain end 4.6 ppm}} \cdot M_{\text{VAc}} + M_{\text{X}}$.

^e Determined by GPC(DMF, 1 mL/min, 40°C) calibrated against PMMA standard.

separated polymer was purified by repeated dissolution in THF and precipitation from hexane twice and finally was dried under vacuum at 50°C for 20 h. The M_n (NMR), M_n (GPC), and PDI of the obtained polymer were 2700 g mol⁻¹, 5000 g mol⁻¹, and 1.12, respectively.

Homo-chain extension experiment using PVAc-X1

In a dry Schlenk tube containing a Teflon-coated magnetic bar, a mixture of 0.1 g [0.037 mmol, M_n (NMR) = 2700 g mol⁻¹, PDI = 1.12] PVAc-X1 macroRAFT agent, and 0.7 mg (0.004 mmol) AIBN were dissolved in 0.5 mL DMF and purged with dry nitrogen gas for 30 min, and then 185 μL (172.2 mg, 2 mmol) VAc, which was already purged with nitrogen, was added during nitrogen purging, and mixed thoroughly. The polymerization tube was then placed in a thermostated bath at 60°C for 24 h. The reaction was stopped by cooling with liquid N₂. The resulting polymerization mixture was dissolved in 2 mL THF, and precipitated from 50 mL hexanes. The precipitated polymer was collected by centrifugation. The separated polymer was further purified by repeated dissolution in THF and precipitation from hexane twice and finally was dried under vacuum at 50°C for 20 h. The observed gravimetric yield was 14%. The M_n (GPC) and PDI of the obtained polymer were 5200 g mol⁻¹, and 1.30, respectively.

Synthesis of poly(vinyl acetate)-*b*-poly(*N*-vinyl pyrrolidone) using PVAc-X1

In a dry Schlenk tube containing a Teflon-coated magnetic bar, 0.1 g [0.037 mmol, M_n (NMR) = 2700 g mol⁻¹, PDI = 1.12] PVAc-X1 macroRAFT agent, 213.7 μL (222.3 mg, 2 mmol) NVP, and 0.7 mg (0.004

mmol) AIBN were dissolved in 2.0 mL DMF, and was purged with dry nitrogen gas for 30 min. The polymerization tube was then placed in a thermostated bath at 60°C for 24 h. The reaction was stopped by cooling with liquid N₂. The product obtained was dissolved in 2 mL THF, and precipitated from 50 mL hexanes. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF, and precipitation from hexane twice and finally dried under vacuum at 50°C for 20 h. The resulting polymer was dispersed in water, which is a solvent for PNVP homopolymer formed, but nonsolvent for poly(vinyl acetate)-*b*-poly(*N*-vinyl pyrrolidone), and the insoluble part was collected by centrifugation. Above procedure was repeated twice and finally dried under vacuum at 50°C for 20 h. This block copolymer was soluble in ethyl acetate and may contain unreacted PVAc homopolymer as impurity. The observed gravimetric yield of PVAc-*b*-PNVP was 27%. The M_n (GPC) and PDI of the obtained polymer were 5400 g mol⁻¹, and 1.16, respectively.

RESULTS

The bulk polymerizations of VAc under different conditions using two xanthate mediators X1 and X2 have been performed. Polymerization conditions and the characterization data of all PVAc samples prepared are shown in Table I. In Run 1, bulk polymerization of VAc using X1 mediator has been carried out by maintaining molar ratios [VAc] : [X1] : [AIBN] = 100 : 1 : 0.2 at 60°C for 3 h. Monomer conversion is about 87%. Calculated theoretical molecular weight [M_n (theor)] (7700 g mol⁻¹) of the formed polymer is close to the corresponding molecular

weight calculated from its $^1\text{H-NMR}$ [$M_n(\text{NMR})$] (7400 g mol^{-1}). The corresponding molecular weight determined by GPC [$M_n(\text{GPC})$] ($13,500 \text{ g mol}^{-1}$) using PMMA standards is almost double with respect to its $M_n(\text{theor})$ or, $M_n(\text{NMR})$ values, while the observed PDI is around 1.30. Under the same experimental conditions, polymerization of VAc using X2 mediator results in the formation of the polymer having $M_n(\text{GPC})$ of 13600 g mol^{-1} with slightly higher PDI of 1.35 at $\sim 67\%$ monomer conversion after 4 h (Run 2). Like Run 1, the corresponding $M_n(\text{theor})$ (6200 g mol^{-1}) of the formed polymer is also close to the $M_n(\text{NMR})$ (6100 g mol^{-1}) and is almost half of the observed $M_n(\text{GPC})$ value. When the monomer concentration increases to 150 equivalent keeping other conditions remained unchanged like Runs 1 and 2, the observed polymer yields are about 86 and 84% for X1 (Run 3) and X2 (Run 4) systems, respectively. In both runs, the molecular weights of the resulting polymers increase as expected. The corresponding $M_n(\text{theor})$ and $M_n(\text{NMR})$ values deviate slightly from each other and is higher for X2 system. The corresponding $M_n(\text{GPC})$ values are almost double with respect to their corresponding $M_n(\text{theor})$ or, $M_n(\text{NMR})$ values. The corresponding PDI values increase, and the observed PDI is higher for X2 system. When the monomer concentration increases further to 300 equivalent keeping other conditions remained almost unchanged like Runs 1 and 2 (Table I), the observed polymer yields were about 88% after 4 h for X1 mediator system (Run 5) and 80% after 5 h for X2 mediator system (Run 6). For both runs, like Runs 3 and 4, the molecular weights increase as expected. The corresponding $M_n(\text{theor})$ and $M_n(\text{NMR})$ values deviate slightly more from each other and is also higher for X2 system (Run 6). The corresponding $M_n(\text{GPC})$ values are almost double with respect to their corresponding $M_n(\text{theor})$ or, $M_n(\text{NMR})$ values. The corresponding PDI values also increase, and the observed PDI is also higher for X2 system (run 6). For X1 system, with a further increase of the monomer loading to 700 equivalent, the observed polymer yield is about 70% (Run 7) and the similar trend of increments of molecular weights and PDI is observed. In order to study the effect of the temperature, polymerizations have also been carried out at 40 and 50°C (Runs 8 and 9, respectively) using X1 as xanthate mediator keeping all other conditions similar to the Run 1. For Run 8, the observed polymer yield is low (70%) after 36 h. The corresponding $M_n(\text{theor})$ (6200 g mol^{-1}) and $M_n(\text{NMR})$ (4700 g mol^{-1}) values are low and deviate more from each other with respect to that of Run 1. The corresponding $M_n(\text{GPC})$ value ($10,800 \text{ g mol}^{-1}$) is almost double with respect to their corresponding $M_n(\text{theor})$ or, $M_n(\text{NMR})$ value. But, the correspond-

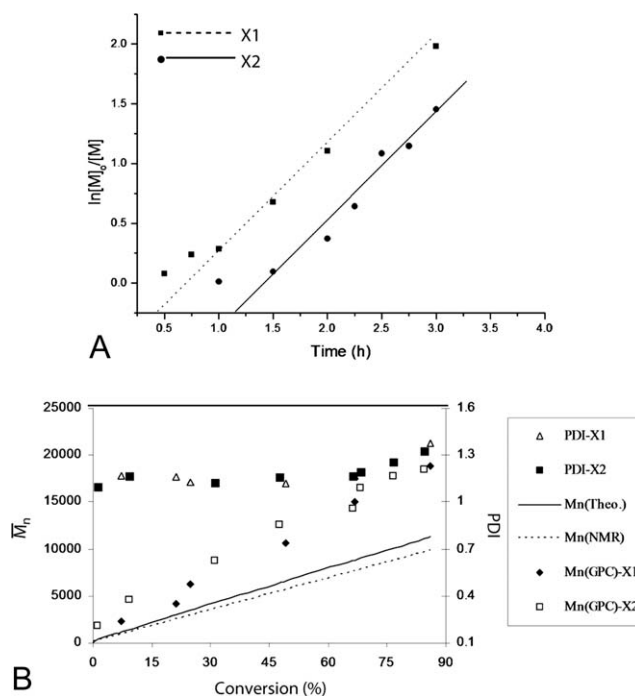


Figure 1 A: Plots of time vs. $\ln[M_0]/[M]$ (where $[M_0]$ = concentration of the monomer at time $t = 0$ min and $[M]$ = concentration of the monomer at the corresponding time). B: Plots of number-average molecular weight M_n and polydispersity (PDI) vs. monomer conversion in the bulk polymerization of vinyl acetate using $[\text{VAc}] = 54.2 \text{ mmol}$, $[\text{X}] = 0.36 \text{ mmol}$ and $[\text{AIBN}] = 0.072 \text{ mmol}$ at 60°C .

ing PDI value is low (1.18) with respect to that of Run 1. For Run 9, the observed polymer yield is 87% after 9 h. The corresponding $M_n(\text{theor})$ (7700 g mol^{-1}) and $M_n(\text{NMR})$ (6000 g mol^{-1}) values are high, and deviate less from each other with respect to that of Run 8, but higher than that of Run 1. The corresponding $M_n(\text{GPC})$ value ($11,400 \text{ g mol}^{-1}$) is almost double with respect to their corresponding $M_n(\text{theor})$ or, $M_n(\text{NMR})$ value. The corresponding PDI value is low (1.25) with respect to that of Run 1, but higher than that of Run 8. Therefore, the bulk polymerization of VAc with molar ratio $[\text{VAc}] : [\text{X}] : [\text{AIBN}] = 100 : 1 : 0.2$ using X1 mediator gave best result in controlling molecular weight at 60°C .

To check the living nature of the polymerization system, a kinetic study of the bulk polymerization of VAc at 60°C was carried out using both X1 and X2 mediators with $[\text{VAc}] : [\text{X}] : [\text{AIBN}] = 150 : 1 : 0.2$. Figure 1(A) shows the plots of the $\ln[M_0]/[M]$ vs. time for X1 and X2 mediators, respectively. Observed induction periods were about 20 and 80 min for X1 and X2 systems, respectively. But, the observed polymerization rate was almost comparable for both systems under the experimental conditions. The plots were linear for both systems up to around 85% conversions. Figure 1(B) shows the

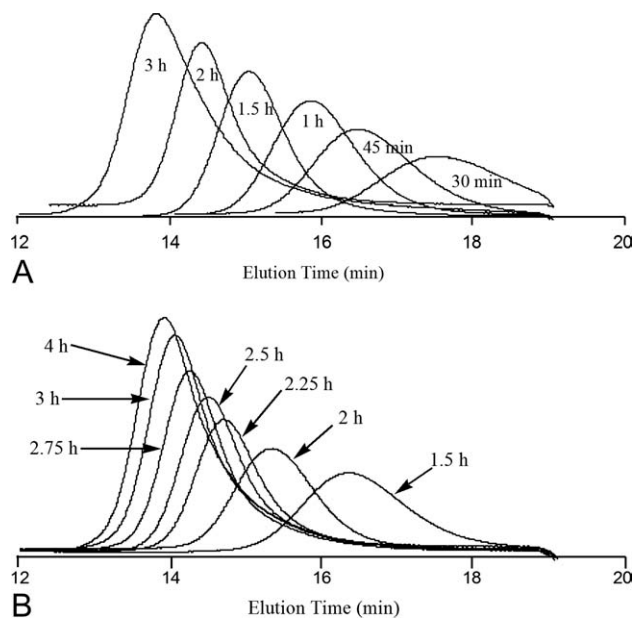


Figure 2 Gradual shifting of the Gel Permeation Chromatograms in the kinetic study of the bulk polymerization of vinyl acetate using at 60°C (A) [VAc] = 54.2 mmol, [X1] = 0.36 mmol and [AIBN] = 0.072 mmol and (B) using [VAc] = 65.1 mmol, [X2] = 0.43 mmol and [AIBN] = 0.08 mmol.

corresponding plots of M_n (GPC), M_n (theor) and PDI vs. monomer conversion (%) using X1 and X2 mediators. The observed molecular weight increased linearly with conversion up to 85% conversion. But the observed molecular weights drifted gradually from the corresponding theoretical values with gradual increase in conversion. The corresponding PDI of the resulting polymers remained almost constant at ~ 1.2 up to $\sim 65\%$ monomer conversion and then increased gradually with a further increase in the monomer conversion. Figure 2(A,B) show the corresponding gradual peak shifting of the GPC chromatograms of these kinetic studies using X1 and X2 mediators, respectively.

Figure 3 shows the end-group analysis of PVAc sample, having M_n (GPC) = 5000 g mol⁻¹ with PDI = 1.12, obtained by the bulk polymerization of VAc using [VAc] : [X1] : [AIBN] = 150 : 1 : 0.2 at 60°C for 30 min, by ¹H-NMR (300 MHz) spectroscopy in CDCl₃ solvent. Peaks (*e*, *e'*, *f*, *f'*, *g*, and *g'*) are the characteristic repeating unit of the VAc as assigned in the figure. The remaining peaks are from the X1 mediator. All 2-ethyl propionate protons (*a*, *b*, *c*, *d*) are observed at around 1.25, 4.63, 3.68, and 1.42 ppm, respectively. In addition, *O*-ethyl protons (*h*, *i*) are observed at 4.12 and 1.16 ppm, respectively. The peak of the methine proton "*f*" of the terminal VAc group close to *O*-ethylxanthate group is observed at around 6.63 ppm. The number average degree of polymerization for this polymer was calculated by

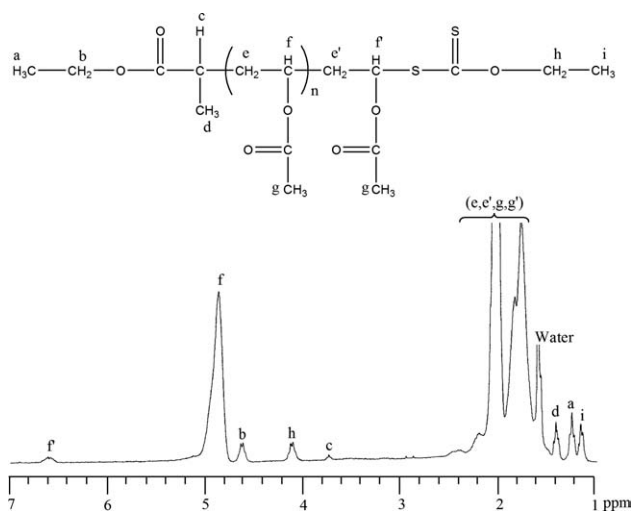


Figure 3 ¹H-NMR spectrum of (300 MHz, CDCl₃) of poly(vinyl acetate) prepared in the bulk polymerization of vinyl acetate using [VAc] = 54.2 mmol, [X1] = 0.36 mmol and [AIBN] = 0.72 mmol at 60°C for 30 min.

dividing the twice the peak area of "*f*" by the peak area of "*h*" or "*b*". The corresponding M_n (NMR) was 2700 g mol⁻¹, which is less than the value (5000 g mol⁻¹) obtained by GPC measurement calibrated against poly(methyl methacrylate) standards.

Figure 4 shows the end-group analysis of PVAc sample, having M_n (GPC) = 5700 g mol⁻¹ with PDI = 1.15, obtained by the bulk polymerization of VAc using [VAc] : [X2] : [AIBN] = 150 : 1 : 0.2 at 60°C for 75 min, by ¹H-NMR (300 MHz) spectroscopy in CDCl₃ solvent. Peaks (*d*, *d'*, *e*, *e'*, *f*, and *f'*) are the characteristic repeating unit of the VAc as assigned in the figure. The remaining peaks are from the X2 mediator. All 2-ethyl propionate protons (*a*, *b*, *c*) are observed at around 1.25, 4.63, and 1.42 ppm,

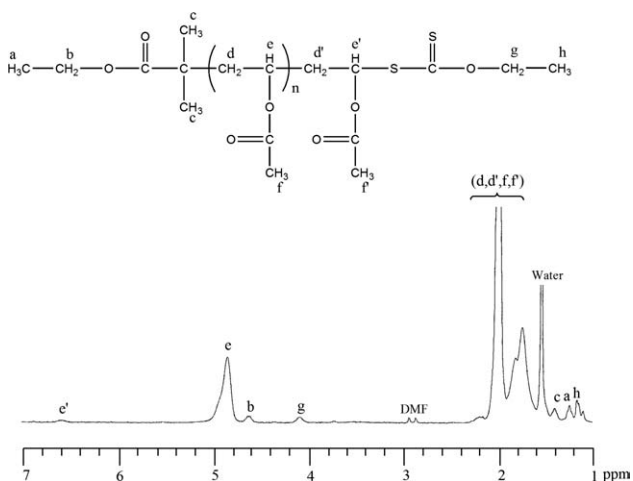


Figure 4 ¹H-NMR spectrum of (300 MHz, CDCl₃) of poly(vinyl acetate) prepared in the bulk polymerization of vinyl acetate using [VAc] = 65.1 mmol, [X2] = 0.43 mmol and [AIBN] = 0.087 mmol at 60°C for 75 min.

TABLE 2
Chain-Extension Experiment^a

Run	Monomer (equiv)	Macro-RAFT agent ^b [$M_n(\text{NMR})/\text{PDI}$]	Yield (%) ^c (Grav.)	M_n (Theor) ^d	M_n (NMR)	\bar{M}_n/PDI (GPC) ^e	X_{VAc} (NMR) ^f	X_{VAc} (GPC) ^f
1	VAc (54)	(1) (2700/1.12)	14	3600	2700	5200/1.30	–	–
2	NVP (54)	(1) (2700/1.12)	27	4300	2800	5400/1.16	0.96	0.93
3	NVP (74)	(2) (3700/1.15)	22	5500	3800	6100/1.20	0.97	0.94

^a Using AIBN : macro-RAFT agent in the ratio 0.2 : 1 equiv in 0.5 mL DMF at 60°C for 24 h.

^b Macro-RAFT agent used was PVAc-X1 = (1) and PVAc-X2 = (2).

^c Conversion was determined gravimetrically.

^d $M_n(\text{Theor}) = M_n(\text{NMR})$ of macro-RAFT agent + ([Monomer]₀/[Macro-RAFT agent]₀) × fraction conversion of monomer × mol. wt. of monomer.

^e Determined by GPC (DMF, 1 mL/min, 40 °C) calibrated against PMMA standard.

^f X_{VAc} = mole fraction of VAc.

respectively. In addition, *O*-ethyl protons (*g*, *h*) are observed at 4.09, and 1.17 ppm, respectively. The peak of the methine proton “*e*” of the terminal VAc group close to *O*-ethylxanthate group is observed at around 6.63 ppm. The number average degree of polymerization for this polymer was calculated by dividing the twice the peak area of “*e*” by the peak area of “*g*” or “*b*”. The corresponding $M_n(\text{NMR})$ was 3700 g mol⁻¹, which less than the value (5700 g mol⁻¹) obtained by GPC measurement calibrated against poly(methyl methacrylate) standards.

Table II shows the results of the homo- and hetero-chain extension experiments using PVAc-X1 macro-RAFT agent [$M_n(\text{NMR}) = 2700$ g mol⁻¹, $M_n(\text{GPC}) = 5000$ g mol⁻¹, PDI = 1.12] (Runs 1 and 2, respectively) and the hetero-chain extension experiments using PVAc-X2 [$M_n(\text{NMR}) = 3700$ g mol⁻¹, $M_n(\text{GPC}) = 5700$ g mol⁻¹, PDI = 1.15] (Run 3) as macroRAFT agent. Homo-chain extension experiment (Run 1) was performed in DMF using [VAc] : [PVAc-X1] : [AIBN] = 54 : 1 : 0.2 at 60°C for 24 h with 14% monomer conversion. The observed $M_n(\text{GPC})$ and PDI of the resulted polymer was 5,200 g mol⁻¹, and 1.30, respectively. Similar observation of negligible molecular weight increase also occurred for the homo-chain-extension experiment starting with PVAc-X2 (not included here). Moreover, the block copolymerization of the PVAc-X1 with NVP was also carried out in DMF using [NVP] : [PVAc-X1] : [AIBN] = 54 : 1 : 0.2 at 60°C for 24 h with 27% monomer conversion (Run 2). The observed $M_n(\text{GPC})$ and PDI of the obtained block copolymer were 5400 g mol⁻¹, and 1.16, respectively. Figure 5(A) shows the corresponding GPC chromatograms for the hetero-chain extension experiments. It clearly shows a small shift of the GPC chromatograms towards high molecular weight. Similarly, the block copolymerization of the PVAc-X2 with NVP carried out in DMF using [NVP] : [PVAc-X2] : [AIBN] = 74 : 1 : 0.2 at 60°C for 24 h resulted with 22% monomer conversion (Run 3). The observed $M_n(\text{GPC})$ and

PDI of the resulting block copolymer were 6100 g mol⁻¹, and 1.20, respectively. Figure 5(B) shows the corresponding GPC chromatograms for the hetero-chain extension experiments. It also clearly shows a small shift of the GPC chromatograms towards high molecular weight. The corresponding $M_n(\text{NMR})$ values of these resultant polymers also support these results of negligible chain-extension. Moreover, the ¹H-NMR spectra of these block copolymers [Fig. 6(A) (from PVAc-X1) and 6B (from PVAc-X2)] in CDCl₃ solvent showed clearly, in addition to the

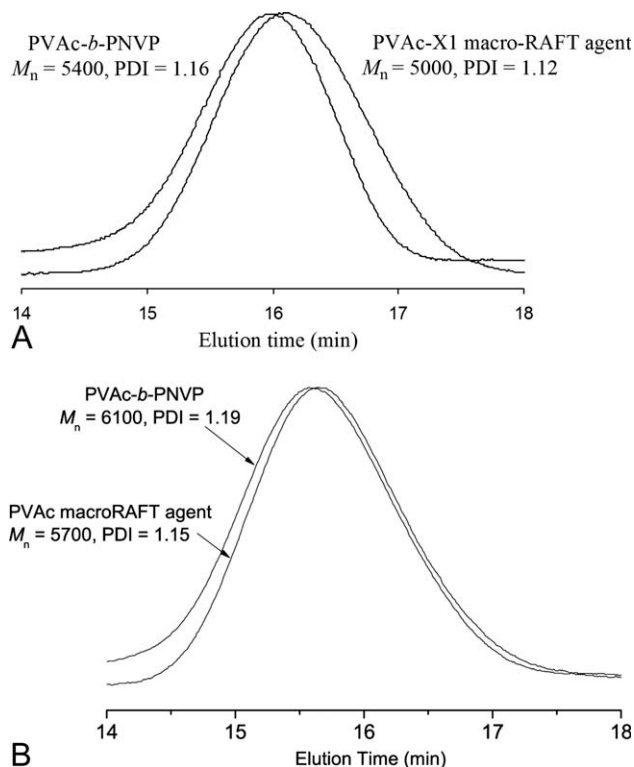


Figure 5 Gel permeation chromatograms of poly(vinyl acetate) macroRAFT agent and the resulted poly(vinyl acetate)-*b*-*N*-vinylpyrrolidone in the hetero-chain extension experiment using (A) PVAc-X1 as macroRAFT agent and (B) PVAc-X2 as macroRAFT agent.

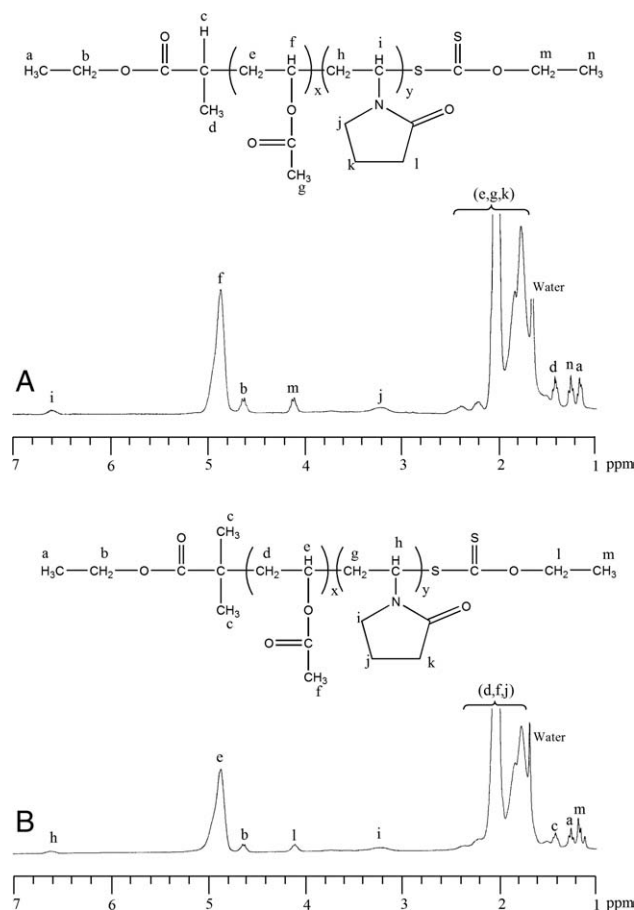


Figure 6 $^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3) of poly(vinyl acetate)-*b*-poly(*N*-vinylpyrrolidone) using (A) PVAc-X1 and (B) PVAc-X2, respectively.

characteristic peaks of the PVAc block, the presence of an additional peak of the proton “*j*” and “*i*” of NVP ring at around 3.2 ppm, which was absent in both PVAc-X1 and PVAc-X2 macroRAFT agent (Figs. 3 and 4, respectively). The observed mole fractions of PVAc block in these block copolymers were 0.96 (Run 2), and 0.97 (Run 3) [calculated on the basis of $M_n(\text{GPC})$ of the corresponding block copolymer and the macroRAFT agent], respectively and 0.93 (Run 2), and 0.94 (Run 3) (calculated on the basis of the $^1\text{H-NMR}$ of these block copolymers), respectively (Table II).

DISCUSSION

Controlled bulk polymerization of VAc with a considerable yield (87%) occurs at 60°C for 3 h using molar ratio $[\text{VAc}] : [\text{X1}] : [\text{AIBN}] = 100 : 1 : 0.2$ resulting in the formation of PVAc having $M_n(\text{theor}) = 7700 \text{ g mol}^{-1}$, $M_n(\text{NMR}) = 7400 \text{ g mol}^{-1}$, $[M_n(\text{GPC}) = 13500 \text{ g mol}^{-1}]$ and $\text{PDI} = 1.30$ (*vide* Run 1, Table I). Earlier-work by Mahanthappa et al.¹⁵ reported the controlled polymerization of VAc using molar ratio $[\text{X1}] : [\text{AIBN}] = 10 : 1$ without mention-

ing the polymerization time. Our finding of a lower molar ratio $[\text{X1}] : [\text{AIBN}] = 5 : 1$ will be useful for the controlled radical polymerization of VAc. Furthermore, the corresponding polymerization using X2 as xanthate RAFT agent for the longer time (4 h) leads to the formation of polymer with lower $M_n(\text{theor}) = 6200 \text{ g mol}^{-1}$, $M_n(\text{NMR}) = 6100 \text{ g mol}^{-1}$, $[M_n(\text{GPC}) = 13600 \text{ g mol}^{-1}]$ and slightly higher PDI (1.35) at lower monomer conversion (67%) (Run 2, Table I). These results strongly indicate the slower reactivity of X2 system than X1 system. Again, the time dependent kinetics study of the bulk polymerization of VAc using both xanthate mediators under the similar experimental conditions at 60°C [Fig. 1(A)] reveal the longer induction period for X2 system (~ 80 min) than X1 system (~ 20 min) although the polymerization rates are almost comparable for both xanthate systems. This result clearly supports the slower reactivity of X2 system with respect to X1 system although their reactivities toward the propagation are almost comparable. This may have been due to the slower reactivity of the stable tertiary carbon centered radical formed from X2 with respect to the relatively unstable secondary carbon centered radical formed from X1. This may also have been responsible for the observed higher PDI in case of X2 system with respect to X1 system. Similar type of observation was also observed by us in the RAFT polymerization of NIPAM.³⁰ Kinetics study [Fig. 1(B)] also reveal that the pseudo-first order kinetics are followed up to 85% monomer conversion and the corresponding molecular weights of the resulting polymers increase linearly with the increase in the monomer conversion up to 85%. The observed $M_n(\text{NMR})$ values slightly drift (gradually decrease) from the corresponding $M_n(\text{theor})$ with the increase in the monomer conversion. Moreover, the observed $M_n(\text{GPC})$ values drift (gradually increase) significantly from the corresponding $M_n(\text{theor})$ values with the increase in the monomer conversion. This result may be mainly due to the chain-transfer reaction to polymer, which eventually leads to the formation of graft polymer, apart from the chain-transfer to monomer. The observed $M_n(\text{GPC})$ values are almost double with respect to that of the corresponding $M_n(\text{theor})$ or, $M_n(\text{NMR})$. The observed difference in $M_n(\text{GPC})$ and $M_n(\text{NMR})$ is due to the use of PMMA standards for calibration. Moreover, in the kinetics study, the corresponding PDI of the resulting polymers remains almost constant around 1.2 up to $\sim 65\%$ monomer conversion and then increases gradually with the further increase in the monomer conversion. This result indicates that the concentration of the propagating radical species initially remains almost constant up to 65% conversion and then decreases slowly with the increase in the monomer conversion. Moreover, the chain-end analyses of

the PVAc-X1 macroRAFT agent, having $M_n(\text{GPC}) = 5000 \text{ g mol}^{-1}$ and $\text{PDI} = 1.12$ obtained at 11.5% monomer conversion and the PVAc-X2 macroRAFT agent, having $M_n(\text{GPC}) = 5700 \text{ g mol}^{-1}$ and $\text{PDI} = 1.15$ obtained at 14.5% monomer conversion, by $^1\text{H-NMR}$ reveal that for both xanthate mediator systems, a single PVAc polymer chain was formed from one molecule of xanthate mediator. But the calculated $M_n(\text{NMR})$ values (2700 and 3700 g mol^{-1} , respectively for X1 and X2 systems) were higher than the corresponding $M_n(\text{theor})$ values (1700 and 2100 g mol^{-1} , respectively for X1 and X2 systems). This may be due to the loss of the xanthate moieties from the polymer chain-end during work up. All these results clearly support the living nature of the polymerization system.

With the further increase in the monomer loading for both xanthate systems (Runs 3–7, Table I), molecular weights increase as expected. The gradual drifting of the corresponding $M_n(\text{NMR})$ or $M_n(\text{GPC})$ from the corresponding $M_n(\text{theor})$ and the observed increase of the corresponding PDI of the resulting polymers with the increase in the monomer loading for both xanthate systems (Runs 3–7, Table I) suggest the higher chain-transfer reactions to monomer and polymer apart from the formation of dead polymer due to the loss of xanthate moieties from the chain-end. Polymerization of VAc using X1 at 40°C for 36 h (Run 8, Table I) results lower polymer yield (70%) with lower $M_n(\text{NMR})$ (4700 g mol^{-1}) value which deviates considerably from the corresponding $M_n(\text{theor})$ (6200 g mol^{-1}) with respect to that of in Run 1. But, the corresponding PDI value is low (1.18) with respect to that in Run 1. Moreover, the polymerization at 50°C for 9 h (Run 9, Table I) results higher polymer yield (87%) with higher $M_n(\text{NMR})$ (6000 g mol^{-1}) value which deviates less from the corresponding $M_n(\text{theor})$ (7700 g mol^{-1}) with respect to that of in Run 1. The corresponding PDI value is low (1.25) with respect to that of Run 1, but higher than that of Run 8. Formation of low concentration of radical species and slow polymerization rate at lower temperature are presumably responsible such results observed in Runs 8 and 9. Thus, the bulk polymerization of VAc with molar ratio $[\text{VAc}] : [\text{X}] : [\text{AIBN}] = 100 : 1 : 0.2$ using X1 mediator gave best result in controlling molecular weight at 60°C (Run 1).

Finally, the observed almost negligible homo-chain and hetero-chain extension involving copolymerization with NVP using both PVAc-X1 and PVAc-X2 macroRAFT agents may be due to the inactivation of the chain-end under the present experimental conditions. It is to be noted here that chain-extension experiments of PVAc-X macroRAFT agent are not included in similar types of reported work.^{15,24}

CONCLUSION

Thus, (S)-2-(Ethyl propionate)-(O-ethyl xanthate) (X1) and (S)-2-(Ethyl isobutyrate)-(O-ethyl xanthate) (X2) are successfully used as RAFT agents for the radical polymerization of VAc. The former shows better chain transfer ability in the polymerization at 60°C. Kinetic study with both RAFT agents shows the pseudo-first order kinetics up to around 85% monomer conversion. Molecular weight of the resulting polymer increases linearly with the increase in the monomer conversion up to around 85%. The observed $M_n(\text{NMR})$ s are close to the corresponding $M_n(\text{theor})$. The corresponding PDI of the resulting polymers remains almost constant around 1.2 up to $\sim 65\%$ monomer conversion and then increases gradually with further increase in the conversion. Chain-end analysis of the resultant polymers by $^1\text{H-NMR}$ clearly shows that the polymerization starts with the radical forming out of the xanthate mediator. The negligible homo-chain extension and also the hetero-chain extension involving synthesis of poly(VAc)-*b*-poly(NVP) diblock copolymer are occurred.

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