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Synthesis of Alkyne-Terminated Xanthate RAFT Agents and Their Uses for the Controlled Radical Polymerization of *N*-Vinylpyrrolidone and the Synthesis of Its Block Copolymer Using Click Chemistry

Vijay Kumar Patel,[1] Niraj Kumar Vishwakarma,[1] Avnish Kumar Mishra,[1] Chandra Sekhar Biswas,[1] Pralay Maiti,[2] Biswajit Ray[1]
[1]Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
[2]School of Material Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, India
Correspondence to: B. Ray (E-mail: biswajitray2003@yahoo.co.in)

ABSTRACT: Two new alkyne-terminated xanthate reversible addition-fragmentation chain-transfer (RAFT) agents: (*S*)-2-(Propynyl propionate)-(*O*-ethyl xanthate) (X_3) and (*S*)-2-(Propynyl isobutyrate)-(*O*-ethyl xanthate) (X_4) were synthesized and characterized and used for the controlled radical polymerization of *N*-vinylpyrrolidone (NVP). X_3 showed better chain transfer ability in the polymerization at 60°C. Molecular weight of the resulted polymer increased linearly with the increase in monomer loading. Kinetics study with X_3 showed the pseudo-first order kinetics up to 67% monomer conversion. Molecular weight (M_n) of the resulting polymer increased linearly with the increase in the monomer conversion up to around 67%. With the increase in the monomer conversion, polydispersity of the corresponding poly(NVP)s initially decreased from 1.34 to 1.32 and then increased gradually to 1.58. Chain-end analysis of the resulting polymer by ^{1}H-NMR and FTIR showed clearly that polymerization started with radical forming out of xanthate RAFT agent. Living nature of the polymerization was also confirmed from the successful homo-chain extension experiment and the hetero-chain extension experiment involving synthesis of poly(NVP)-*b*-polystyrene amphiphilic diblock copolymer. Formed alkyne-terminated poly(NVP) also allowed easy conjugation to azide-terminated polystyrene by click chemistry to prepare well-defined poly(NVP)-*b*-polystyrene block copolymers. Resulting polymers were characterized by GPC, ^{1}H-NMR, FTIR, and thermal study. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: alkyne-terminated xanthate RAFT agent; RAFT polymerization; *N*-vinylpyrrolidone; poly(NVP)-*b*-polystyrene; click chemistry

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INTRODUCTION

Because of its high water solubility, low toxicity, biocompatibility, complexation capability, cryo-protectivity, lypo-protectivity, and antibiofouling properties poly(*N*-vinylpyrrolidone) (PNVP) was used widely in chemical and medical applications.[1,2] *N*-vinylpyrrolidone (NVP) was usually polymerized by radical polymerization owing to the non-conjugation of its amidic keto group with the vinyl group. Controlled synthesis of its homopolymer and block-copolymers were explored using different controlled/living radical polymerization methods.[3–14] Kamigaito et al.[5] reported the controlled radical polymerization of NVP as well as the simultaneous control of molecular weight and tacticity of PNVP through RAFT polymerization in fluoroalcohols using xanthate type RAFT agents. Later, Gnanou et al.[6] reported the controlled radical polymerization of NVP using dithiocarbamate type RAFT agents. Hadjichristidis et al.[7] also reported the controlled radical polymerization of NVP using Nitroxide-mediated and RAFT polymerization methods. Yamago et al. reported the synthesis of highly controlled PNVP homopolymers and its block copolymers using organostibine[8,9] organotellurium,[10] and organobismuthine[11] mediators. Cu-metal catalyzed ATRP of NVP was recently reported by Lu et al.[12] using 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradecane (Me_6cyclam) as ligand in 1,4-dioxane/isopropanol mixture. Recently, Klumperman et al.[13] studied comprehensively the mechanistic aspect of the xanthate mediated RAFT polymerization of NVP. The same group also reported[14] the preliminary results on the homopolymerization of NVP using (*S*)-2-(Ethyl propionate)-(*O*-ethyl xanthate) (X1) in the presence of poly(ethylene glycol) monomethyl ether and also the synthesis of double hydrophilic block copolymer of PNVP and poly(ethylene glycol) (PEG) starting with the

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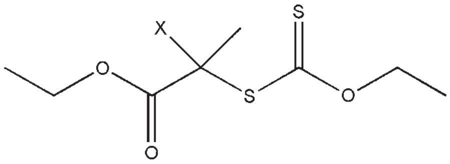
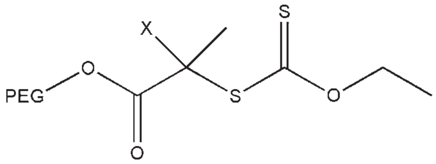
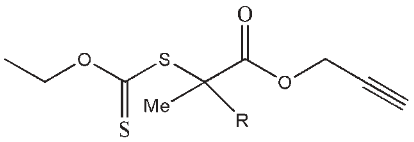


(a) X = H (**X1**), CH_3 (**X2**)



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



(c) R= H, (*S*)-2-(Propynyl propionate)-(*O*-ethyl xanthate) (**X_3**)
R= CH_3, (*S*)-2-(Propynyl isobutyrate)-(*O*-ethyl xanthate) (**X_4**)

Scheme 1. Structures of RAFT Agents.

xanthate X_1 having a poly(ethylene glycol) (PEG) segment (PEG-X1 macroinitiator) (Scheme 1).Very recently, we have reported the synthesis of one new xanthate RAFT agent (*S*)-2-(Ethyl isobutyrate)-(*O*-ethyl xanthate) (X_2) [Scheme 1(a)] and studied in detail the polymerization of NVP using X_1 and X_2 RAFT agents.[15] But, homo-/hetero-chain-extension experiment with the corresponding PNVP-xanthate macro-RAFT agent leads to a little increase in chain length. In order to solve this problem, we plan to synthesize an alkyne containing xanthate RAFT agent, which can polymerize NVP in controlled way and also the resulting well-defined alkyne terminated PNVP can also combine to any azide-terminated polymer to make its corresponding block copolymer. Here, we report the synthesis and characterization of two new alkyne containing xanthate RAFT agents, namely, (*S*)-2-(Propynyl propionate)-(*O*-ethyl xanthate) (X_3) and (*S*)-2-(Propynyl isobutyrate)-(*O*-ethyl xanthate) (X_4) [Scheme 1(c)] and studied the usefulness of the same for the controlled RAFT polymerization of NVP. Moreover, we also report the efficient synthesis of polystyrene-*b*-PNVP through click chemistry.

EXPERIMENTAL

Materials

2-bromopropionyl bromide (98%, Aldrich, USA), ethyl α-bromoisobutyrate (EBIB) (97%, Aldrich, USA), *N, N, N', N'', N''*-Pentamethyldiethylenetriamine (PMDETA) (99%, Aldrich, USA), $CuBr_2$ (99%, Aldrich, USA), carbon disulfide (95%, Loba Chemie, India), diethyl ether (Laboratory Reagent Grade, s.d.fine, India), hexane (Laboratory Reagent Grade, CDH, India), potassium hydroxide (Qualigens, India), anhydrous magnesium sulfate (Extra Pure, Loba Chemie, India) were used as received. *N*-Vinylpyrrolidone (99%, Aldrich, USA) and Styrene (99%, Aldrich, USA) were dried over anhydrous calcium hydride and distilled under reduced pressure. $2, 2'$- Azobis(isobutyronitrile) (AIBN) (98%, Spectrochem, India) was re-crystallized from methanol. CuBr (98%, Aldrich, USA) was purified by the treatment with acetic acid and then washing with ethanol, Ethanol (Saraya Distilliary, India) and methanol (99%, Loba Chemie, India) was left over CaO for overnight and distilled over fresh CaO. Propargyl alcohol (98%, Loba Chemie, India) was distilled over anhydrous magnesium sulphate. Tetrahydrofuran (99%, Loba Chemie, India) was dried freshly over sodium and benzophenone. Deionized water was prepared by redistillation of the double distilled water in an all-glass distillation apparatus. Synthesis of Potassium O-ethyl xanthate was prepared according to our previous report.[15]

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_2O as solvent and were reported in parts per million (δ) from internal tetramethylsilane (or residual solvent peak). NVP monomer conversion (%) was determined using ^{1}H-NMR spectroscopy in $CDCl_3$ by comparing the integrated peak area of the residual vinylic signals at 4.3–4.4 ppm (2H) and 7.0–7.1 ppm (1H) of the monomer with the peak area of the methylene protons adjacent to "N" of pyrrolidone ring of the corresponding polymer at 3.0–3.4 ppm (2H). The number average molecular weight (M_n) and polydispersity index (PDI) (M_w/M_n) were determined by Younglin ACME 9000 Gel Permeation Chromatography in DMF at 40°C with flow rate 0.5 mL/min on two polystyrene gel columns [PL gel 5 μm 10E 4 Å columns (300×7.5 mm^2)] connected in series to Younglin ACME 9000 Gradient Pump and a Younglin ACME 9000 RI detector. The columns were calibrated against either seven poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10) or seven polystyrene (PSt) standard samples (Polymer Lab, PSt Calibration Kit, S-M2-10). The theoretical number average molecular weight [M_n(theor)] was calculated using the following equation:

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

where, x_{NVP} is the fraction conversion of NVP, M_{NVP} is the molecular weight of NVP and M_{X} is the molecular weight of the xanthate RAFT agent X. Fluorescence measurements were carried out on a Varian Cary Eclipse Fluorescence Spectrometer.

Typical Determination of Critical Micelle Concentration (cmc)[16]

A series of aqueous PNVP-*b*-PSt (run 1, Table III) solutions with concentrations ranging from 1×10^{-4} to 1 mg/mL were prepared by the dilution of a stock solution of block copolymer with deionized water. A pyrene stock solution in acetone was transferred to a series of vials, the acetone was evaporated under nitrogen, and the block copolymer solutions were added to the vials to get a final pyrene concentration of 6×10^{-7} *M* in each vial. After being equilibrated overnight at ambient temperature, the excitation spectra (300–360 nm) of the solutions were recorded at an emission wavelength of 394 nm using slit width of 5 nm. The ratio of the peak intensities of the excitation spectra of pyrene at 337.07 nm ($I_{337.07}$) and 333.07 nm ($I_{333.07}$) was plotted as a function of polymer concentration. The sharp inflection point of two straight lines at lower concentration was noted as the cmc of the block copolymer.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using Mettler TGA thermogravimetric analyzer in the temperature range from 40 to 600°C with a heating rate of 20°C/min under N_2 atmosphere.

Differential Scanning Calorimeter

Differential scanning calorimeter (DSC) measurements were performed using Mettler 832 DSC instrument under N_2 atmosphere. The instrument was calibrated with indium before use. The samples were first heated to 200°C at 10°C/min heating rate and held at this temperature for 5 min to remove the thermal history, followed by quenching to −10°C. A heating rate of 10°C/min was used for second heating run. Results were reported from the second heating run.

Synthesis of *O*-Propynyl-2-bromopropionate

To a solution of the 2-bromopropionyl bromide (5 mL, 10.2 g, 0.05 mol) in dry THF (30 mL) cooled at 0°C under nitrogen, a solution of propargyl alcohol (4 mL, 3.9 g, 0.07 mol) and pyridine (5.6 mL, 5.4 g, 0.07 mol) in dry THF (30 mL) was added drop wise during 10 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The product mixture was washed consecutively with 5% (w/v) aqueous $NaHCO_3$ solution (3 × 75 mL), 8.5% (v/v) aqueous HCl solution (2 × 50 mL), saturated aqueous brine (50 mL) solution, and distilled water (2 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. Distillation provided 5.5 g (56% yield) of the ester. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.84 (d, 3 H), 2.52 (s, 1 H), 4.39 (q, 1 H), 4.76 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 21.5, 39.1, 53.3, 75.6, 77.4, and 169.4. IR (neat): 3290, 2980, 2930, 2130, 1745 cm^{-1}.

Synthesis of (*S*)-2-(Propynyl propionate)-*O*-ethyl xanthate) (X_3)

Potassium *O*-ethyl xanthate (3 g, 0.02 mol) was added to a solution of *O*-propynyl-2-bromopropionate (3.5 g, 0.02 mol) in dry ethanol (20 mL), and stirred for 24 h at room temperature. The resulted white precipitate was filtered off. The filtrate was diluted with diethyl ether (250 mL), and washed three times with deionised water (50 ml). Then, the resulted diethyl ether solution was dried over anhydrous $MgSO_4$, filtered, and solvent was evaporated to dryness. The yellow colored liquid product was purified by column chromatography using hexane/ethyl acetate (95:5 v/v) as the eluent (R_f value = 0.71). A yellow colored oily product (40% yield by NMR) was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.4 (t, 3H, C(S)- OCH_2CH_3), 1.57 (d, 3H, CH_3CH), 2.49 (s,1H,-$CH_2C(CH)$), 4.42 (q, 1H, C(CH_3)CH), 4.62 (q, 2H, C(S)OCH_2), 4.73 (s, 2H, -CH_2C(CH)). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.6, 16.6, 46.7, 53.0, 70.3, 75.3, 77.4, 170.7, 211.6. IR (neat): 3290, 2980, 2930, 2130, 1745 cm^{-1}. Another side product, 2-(*O*-ethylcarbonodithionato)-propionyl-(*O*-ethylcarbonodithionate) (X_3') having R_f value 0.62 was obtained with 28% yield (NMR). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28 (t, 3H, C(S)- OCH_2CH_3), 1.41 (t, 3H, C(O)SC(S) OCH_2CH_3), 1.58 (d, 3H, CH_3CH), 4.21 (q, 2H, C(S)- O$CH_2$$CH_3$), 4.41 (q, 1H, C($CH_3$)CH), 4.67 (t, 3H, C(O)SC(S) O$CH_2$$CH_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.6, 14.1, 16.9, 29.7, 47.2, 61.7, 70.2, 171.4, 212.1. IR (neat): 2983, 2933, 1737 cm^{-1}.

Synthesis of *O*-Propynyl-2-bromoisobutyrate

To a solution of the α-bromoisobutyryl bromide (7.5 mL, 14 g, 0.06 mol) in dry THF (50 mL) cooled to 0°C under nitrogen, a solution of propargyl alcohol (5.2 mL, 5 g, 0.09 mol) and pyridine (7.1 g, 7.2 mL, 0.09 mol) in dry THF (40 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The product mixture was washed consecutively with 5% (w/v) aqueous $NaHCO_3$ solution (3 × 75 mL), 8.5% (v/v) aqueous HCl solution (2 × 50 mL), saturated aqueous brine solution (50 mL), and distilled water (2 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. Distillation provided 6.1 g (49 %) of the ester. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 6 H), 2.51 (s, 1 H), 4.76 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 21.8, 42.2, 53.3, 75.6, 77.4, and 169.4. IR (neat): 3290, 2980, 2930, 2130, 1745 cm^{-1}.

Synthesis of (*S*)-2-(Propynyl isobutyrate)-(*O*-ethyl xanthate (X_4)

Potassium *O*-ethyl xanthate (3 g, 0.02 mol) was added to a solution of *O*-propynyl-2-bromoisobutyrate (3.75 g, 0.02 mol) in dry ethanol (30 mL), and stirred for 24 h at room temperature. The resulted white precipitate was filtered off. The filtrate was diluted with diethyl ether (250 mL), and washed three times with deionised water (50 mL). Then the resulted diethyl ether solution was dried over anhydrous $MgSO_4$, filtered, and solvent was evaporated to dryness. The yellow colored liquid product was purified by column chromatography using hexane/ethyl acetate (95:5 v/v) as the eluent (R_f value = 0.78). A yellow colored oily product (40% yield by NMR) was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.4 (t, 3H, C(S)- OCH_2CH_3), 1.57 (d, 3H, CH_3CH), 2.49 (s,1H,-$CH_2C(CH)$), 4.42 (q, 1H, C(CH_3)CH), 4.62 (q, 2H, C(S)OCH_2), 4.73 (s, 2H, -CH_2C(CH)). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.3, 25.7, 53, 53.8, 69.9, 75, 77.4, 172.4, 210.5. IR (neat): 3286, 2982, 2938, 2129, 1740 cm^{-1}. Another side product, 2-(*O*-ethylcarbonodithionato)-propionyl-(*O*-ethylcarbonodithionate) (X_4') having R_f value 0.67 was obtained with 28% yield (NMR). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28 (t, 3H, C(S)- OCH_2CH_3), 1.41 (t, 3H, C(O)SC(S) OCH_2CH_3), 1.58 (d, 3H, CH_3CH), 4.21 (q, 2H, C(S)- O$CH_2$$CH_3$), 4.41 (q, 1H, C($CH_3$)CH), 4.67 (t, 3H, C(O)SC(S) O$CH_2$$CH_3$).

Typical Xanthate-Mediated Bulk Polymerization of NVP

Desired amount of distilled NVP, recrystallized AIBN, and X_3 RAFT agent were placed in a dry Schlenk tube, and mixed thoroughly, and was purged with dry N_2 gas for 30 min. The flask was immersed in a thermostated oil bath preheated at a definite temperature. Reaction was stopped by freezing the Schlenk tube with liquid N_2 after definite time interval. A small portion of the polymerization mixture was used to determine the monomer conversion by ^{1}H-NMR. The rest of the polymerization mixture was dissolved in THF, and precipitated from excess amount of hexane. The precipitated polymer was separated by centrifugation. The separated polymer was dried under vacuum at 50°C for 12 h.

Polymerization Procedure for the Kinetic Study [NVP : X_3 : AIBN :: 200 : 1 : 0.2]

A mixture of NVP (6 mL, 6.24 g, 56.1 mmol), X_3 (65.4 mg, 0.28 mmol), and AIBN (9.3 mg, 0.057 mmol) were placed in a dry Schlenck tube containing a Teflon-coated magnetic bar, and was purged with dry N_2 gas for 45 min. This degassed stock solution was divided into eight dry and degassed polymerization glass tubes. The polymerization tubes were then placed in a thermostated bath preheated at 60°C for the desired interval. The reaction was stopped by freezing the polymerization mixture with liquid N_2. A small portion of the polymerization mixture was used to determine the monomer conversion (%) by ^{1}H-NMR. Molecular weight (M_n) and its distribution (PDI) of the formed polymer were determined by GPC using a small portion of the polymerization mixture.

Synthesis of Alkyne-terminated Poly(NVP) (PNVP) Macro-RAFT Agent

A mixture of NVP (6 mL, 6.24 g, 56.1 mmol), X_3 (65.4 mg, 0.282 mmol), and AIBN (9.3 mg, 0.057 mmol) were placed in a dry Schlenck tube containing a teflon coated magnetic bar, and was purged with dry N_2 gas for 45 min. The polymerization tube was then placed in a thermostated bath preheated at 60°C for 3 h. The reaction was stopped by freezing the polymerization mixture with liquid N_2. The polymerization mixture was dissolved in THF (5 mL) and precipitated from hexane (200 mL). The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitation from hexane twice, and finally was dried under vacuum at 50°C for 12 h. Monomer conversion (5.4%) was gravimetrically determined. The M_n and PDI of the obtained polymer were observed at 2300 g mol^{-1} and 1.25, respectively, using PMMA standards and 8000 g mol^{-1} and 1.14, respectively, using PSt standards.

Homo-chain Extension Polymerization Method

A mixture of (0.05 g, 0.022 mmol) PNVP macro-RAFT agent (M_n = 2300 g mol^{-1}, PDI = 1.25), (0.7 mg, 0.0044 mmol) AIBN, and (232.5 μL, 0.24 g, 2.2 mmol) NVP in DMF (0.5 mL) was taken in a dry Schlenck tube containing a Teflon-coated magnetic bar, and was purged with dry N_2 gas for 30 min. The polymerization tube was then placed in a thermostated bath preheated at 60°C for 24 h. The reaction was stopped by freezing the polymerization mixture with liquid N_2. The polymerization mixture was dissolved in THF (2 mL) and precipitated from hexane (50 mL). The precipitated polymer was separated by centrifugation. The separated polymer was purified by repeated dissolution in THF, and precipitated from hexane twice, and finally was dried under vacuum at 50°C for 12 h. Monomer conversion (49%) was gravimetrically determined. The M_n and PDI of the obtained polymer were observed at 7000 g mol^{-1} and 2.57, respectively, using PMMA standards.

Synthesis of Poly(*N*-vinylpyrrolidone)-*b*-polyStyrene (PNVP-*b*-PSt) using Alkyne-Terminated PNVP Macro-RAFT Agent

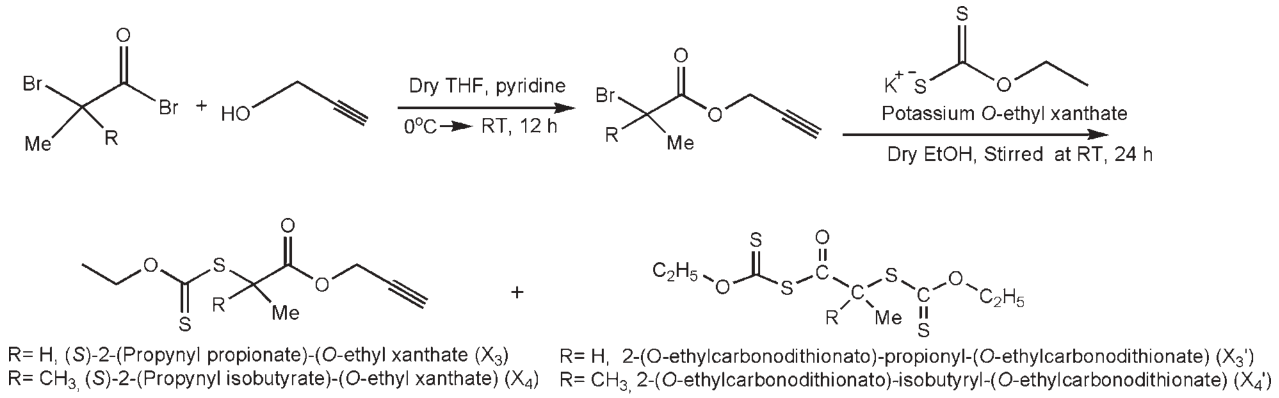
A mixture of (0.05 g, 0.022 mmol) alkyne-terminated PNVP macro-RAFT agent (M_n = 2300 g mol^{-1}, PDI = 1.25), (0.7 mg, 0.0044 mmol) AIBN, and (248.5 μL, 0.23 g, 2.2 mmol) styrene in 0.5 mL DMF was taken in a dry Schlenck tube containing a Teflon-coated magnetic bar, and was purged with dry N_2 gas for 30 min. The polymerization tube was then placed in a thermostated bath preheated at 60°C for 24 h. The polymerization was stopped by freezing the reaction mixture with liquid N_2. Monomer conversion (46%) was determined by ^{1}H-NMR using a small portion of the polymerization mixture. The rest of the polymerization mixture was dissolved in THF (2 mL) and precipitated from hexane (50 mL). The precipitated polymer was separated by centrifugation. The separated polymer was purified by repeated dissolution in THF, and precipitation from diethyl ether thrice, and finally was dried under vacuum at 50°C for 12 h. The dried polymer was again purified by repeated dissolution in THF and precipitation from methanol. The M_n and PDI of the methanol-precipitated polymer were observed at 2800 g mol^{-1} and 1.27, respectively, using PMMA standards and 8200 g mol^{-1} and 1.23, respectively, using PSt standards.

Typical Synthesis of Bromo-Terminated Poly(Styrene) (PSt) Macroinitiator (Run 1, Table S1, Supporting Information)

Freshly distilled styrene (6 mL, 5.454 g, 5.244 × 10^{-2} mol), CuBr (125.4 mg, 8.74 × 10^{-4} mol), $CuBr_2$ (39 mg, 17.48 × 10^{-5} mol) and EBib (128.3 μL, 8.74 × 10^{-4} mol) was placed in a dry Schlenk tube containing a Teflon coated magnetic bar, and mixed thoroughly, and purged with dry N_2 gas for 30 min. To it, nitrogen purged PMDETA (218 μL, 10.49 × 10^{-4} mol) was added under nitrogen during vigorous stirring. The Schlenk tube was immersed in a thermostated oil bath preheated at 80°C. Reaction was stopped by freezing the Schlenk tube with liquid N_2 after the definite time interval. A small portion of the polymerization mixture was used to determine the monomer conversion by ^{1}H-NMR. The rest of the polymerization mixture was purified by repeated dissolution in THF and precipitation from excess amount of methanol thrice. The precipitated polymer was collected by centrifugation. The separated polymer was dried under vacuum at 50°C for 24 h. The M_n and PDI of the methanol-precipitated polymer were observed at 3000 g mol^{-1} and 1.13, respectively, using PMMA standards and 10,200 g mol^{-1} and 1.07, respectively, using PSt standards.

Typical Synthesis of Azide-terminated Poly(styrene) (PSt) (run 1, Table S2, Supporting Information)

Bromo-terminated poly(styrene) macroinitiator (2 g, 1.75 × 10^{-4} mol) was dissolved in 6 mL of dry DMF in a Schlenk tube containing a Teflon coated magnetic bar, and then required amount of NaN_3 (0.2 g, 3.1 × 10^{-3} mol) was added, mixed thoroughly, and purged with dry N_2 for 30 min. The flask was immersed in a thermostated oil bath preheated at 50°C. The polymerization mixture was dissolved in THF, and precipitated from excess amount of methanol. The precipitated polymer was separated by centrifugation. The separated polymer was dried under vacuum at 50°C for 12 h. Yield (gravimetric) = 1.82 g (92%). The M_n and PDI of the resulting polymer were observed at 2900 g mol^{-1} and 1.13, respectively, using PMMA standards and 10,100 g mol^{-1} and 1.07, respectively, using PSt standards.



Scheme 2. Synthesis of Alkyne-terminated Xanthate RAFT Agents.

Typical Synthesis of Poly(*N*-vinylpyrrolidone)-*b*-polystyrene (PNVP-*b*-PSt) using Click Chemistry (Run 1, Table III)

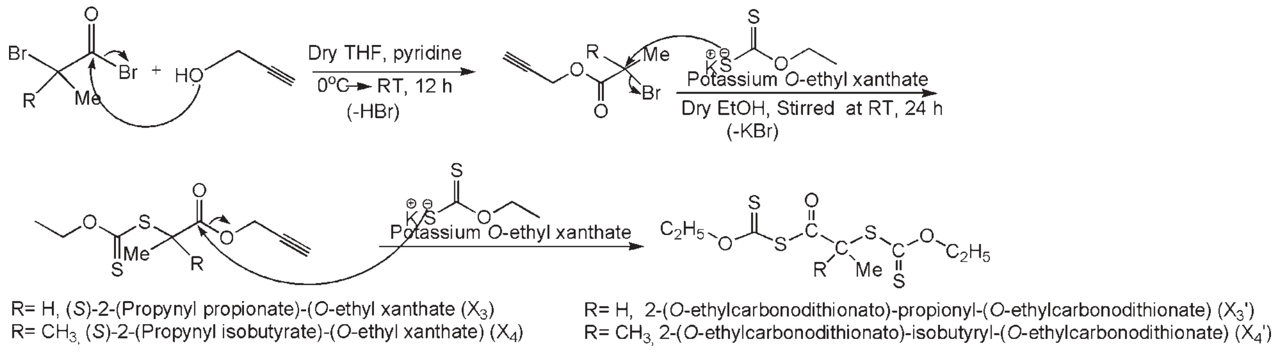
A mixture of (0.05 g, 0.022 mmol) alkyne-terminated PNVP macro-RAFT agent (M_n = 2300 g mol^{-1}, PDI = 1.25), (3.1 mg, 0.022 mmol) CuBr, and (228.3 mg, 0.023 mmol) azide-terminated polystyrene macroinitiator (M_n = 10,100 g mol^{-1}, PDI = 1.07) in DMF (0.5 mL) was taken in a dry Schlenck tube containing a Teflon-coated magnetic bar, and purged with dry N_2 gas for 30 min. The polymerization tube was then placed in a thermostated bath at 80°C for 24 h. The polymerization was stopped by freezing the polymerization mixture with liquid N_2. DMF was evaporated, and then polymerization mixture was dissolved in THF (2 mL). The Cu (I) catalyst was removed by passing through neutral alumina. The filtrate was evaporated till ~ 2 mL THF was left. The polymer was precipitated from 50 mL methanol. The precipitated polymer was collected by centrifugation. The separated polymer was purified by repeated dissolution in THF and precipitation from methanol thrice, and finally was dried under vacuum at 50°C for 24 h. The M_n and PDI of the methanol-precipitated polymer were observed at 3700 g mol^{-1} and 1.40, respectively, using PMMA standards and 13,000 g mol^{-1} and 1.18, respectively, using PSt standards.

RESULTS AND DISCUSSION

Synthesis of Alkyne-Terminated Xanthate RAFT Agents

Alkyne-terminated xanthate RAFT agent (*S*)-2-(Propynyl propionate)-(*O*-ethyl xanthate) (X_3) has been synthesized *via* two steps reaction (Scheme 2): (i) reaction of 2-bromopropionyl bromide with propargyl alcohol to prepare *O*-propynyl-2-bromopropionate followed by the (ii) reaction of *O*-propynyl-2-bromopropionate with potassium *O*-ethyl xanthate.

Second step gives mixture of two products: desired (*S*)-2-(Propynyl propionate)-(*O*-ethyl xanthate) (X_3) and side product (*O*-ethylcarbonodithionato)-propionyl-(*O*-ethylcarbonodithionate) ($X_3^{/}$) with yield ratio 62:38. X_3 and $X_3^{/}$ were separated by silica gel column chromatography using 95:5% (v/v) hexane/ethyl acetate mixtures as eluent with R_f values 0.71 and 0.62, respectively. Similarly, another alkyne-terminated xanthate RAFT agent (*S*)-2-(Propynyl isobutyrate)-(*O*-ethyl xanthate) (X_4) has been synthesized via two-steps reaction starting with α-bromoisobutyryl bromide in place of 2-bromopropionyl bromide. First step involves the formation of *O*-2-propynyl-2-bromoisobutyrate. Second step involves the formation of two products: desired (*S*)-2-(Propynyl-2-bromo-isobutyrate)-(*O*-ethyl xanthate) (X_4) and side product (*O*-ethylcarbonodithionato)-isobutyryl-(*O*-ethylcarbonodithionate) ($X_4^{/}$) with yield ratio 80:20. X_4 and $X_4^{/}$ were separated by silica gel column chromatography using 95:5 % (v/v) hexane/ethyl acetate mixtures as eluent with R_f values 0.78 and 0.67, respectively. All products are characterized by ^{1}H-NMR, ^{13}C-NMR, and FTIR. Probable mechanism for the formation of X_3 or X_4 (Scheme 3) is through the attack of the potassium *O*-ethyl xanthate at the tertiary carbon centered containing Br atom of *O*-propynyl-2-bromopropionate or *O*-2-propynyl isobutyrate, respectively. The formation of $X_3^{/}$ or $X_4^{/}$ is through the attack of



Scheme 3. Probable Mechanism for the Synthesis of Alkyne-terminated Xanthate RAFT Agents.

Table I. RAFT Polymerization of NVP Mediated with X3 and X4 at 60°C[a]

Run	NVP (equiv.)	RAFT agent (equiv.)	Time (h)	Conv. (%)[b]	$M_{n,\text{theo.}}$[c]	$M_{n,\text{GPC}}$[d]	M_w/M_n[d]
1	100	X_3(1)	24	61	7012	7200	1.51
2	100	X_4(1)	40	46	5370	5200	1.58
3	200	X_3(1)	13	64	14,458	16,000	1.48
4	300	X_3(1)	10	55.2	18,637	20,700	1.55
5	500	X_3(1)	21	56	31,351	30,900	1.94

[a] Bulk polymerization using 0.2 equivalent AIBN with respect to RAFT agent, [b] Determined by ^{1}H NMR by comparing the integrated peak area of the residual vinylic signals at 4.3-4.4 ppm (2H) and 7.0-7.1 ppm (1H) of the monomer with the methylene peak of the pyrrolidone ring at 3.0-3.4 ppm (2H) of the residual monomer and the corresponding polymer, [c] $\overline{M}_n(\text{theor}) = \frac{[\text{NVP}]_o}{[X]_o} \cdot x_{\text{NVP}} \cdot M_{\text{NVP}} + M_{\text{X}}$, where, x_{NVP} is the fraction conversion of NVP, M_{NVP} is the molecular weight of NVP and M_{X} is the molecular weight of the xanthate mediator X, [d] Determined by GPC(DMF,0.5 mL/min, 40°C) calibrated against PMMA standard.

another molecule of potassium *O*-ethyl xanthate at the ketonic carbon center of X_3 or X_4. Thus, two new alkyne-terminated xanthate RAFT agents (mediators) X_3 and X_4 have successfully been synthesized and characterized.

Polymerization of NVP

To study the usefulness of the prepared alkyne-terminated xanthate RAFT agents, we have performed the RAFT polymerization of NVP under different conditions. Polymerization conditions and the characterization data of all the polymers prepared are shown in Table I. In run 1, bulk polymerization of NVP has been carried out at 60°C for 24 h using X_3 RAFT agent with molar ratio of [NVP]: [X_3]: [AIBN] = 100:1:0.2. The observed monomer conversion is 61%. The experimental molecular weight [M_n(GPC)] calibrated against PMMA standard (7200 g mol^{-1}) of the resulting polymer is close to the corresponding M_n(theor) (7012 g mol^{-1}) and the corresponding polydispersity is 1.51. Under the similar experimental conditions, polymerization using X_4 RAFT agent has resulted in the formation of lower molecular weight [M_n(theor) = 5370 g mol^{-1}, M_n(GPC) = 5200 g mol^{-1}, PDI = 1.58] polymer at 46% monomer conversion after 40 h. The formation of higher molecular weight polymer with lower PDI at higher yield within shorter polymerization period using X_3 may be due to the higher reactivity of the less stable secondary carbon-centered radical derived from X_3 with respect to the lesser reactivity of the relatively stable tertiary carbon-centered radical derived from X_4. Similar type of results in the xanthate-mediated RAFT polymerization has also been reported in the literature.[5,15,18–21] On further increases of monomer concentration from 100 equiv (Run 1) to 200 equiv (Run 3), 300 equiv (Run 4), and 500 equiv (Run 5) keeping other experimental conditions remained almost same like Run 1, molecular weight of the resulting polymers gradually increases with the increase in the monomer loading as expected. Moreover, the observed M_n(GPC) values are close to the corresponding M_n(theor) values. The corresponding PDI of the resulting polymers are almost constant (at ~ 1.5) with 100 equiv (Run 1) and 200 equiv (Run 3) monomer loadings. Then, it increases slightly (to 1.55) with 300 equiv monomer loading (Run 4). However, the increase is considerable (to 1.94) with 500 equiv monomer loading (Run 5). The observed higher polydispersity in Runs 1 and 3 clearly indicates the formation of dead polymer due to the loss of the xanthate moieties from the growing polymer chain-end or, chain-transfer reaction to the monomer/polymer or, chain transfer reaction to alkyne-group at polymer chain-end. Slight increase in Run 4 may be due to the higher chain-transfer reactions owing to the higher monomer concentrations. Significant increase in Run 5 may be due to the considerable loss of xanthate moieties from the chain-end or, chain-transfer reactions to monomer/polymer owing to the higher contribution of solid state polymerization. Thus, it is clear from the table that polymerization of NVP using X_3 RAFT agent at 60°C resulted with relatively controlled polymerization with higher polymer yield. Therefore, the rest of the polymerizations were performed using X_3 RAFT agent at 60°C.

LIVINGNESS OF THE POLYMERIZATION SYSTEM

Livingness of the NVP polymerization using X_3 RAFT agent was checked by performing the kinetic study of its bulk polymerization at 60°C with molar ratio [NVP]: [X_3]: [AIBN] = 200:1:0.2. The plots of the monomer conversion (%) and $\ln([M_o]/[M])$ vs. time are shown in Figure 1(a). It shows that monomer conversion (%) increases linearly up to around 67% conversion. The corresponding $\ln([M_o]/[M])$ plot is also apparently linear (with slope = 0.093); however, careful analysis shows that $\ln([M_o]/[M])$ plot is initially linear (with slope = 0.051) up to around 20% conversion and then curved up with another linear part (with slope = 0.12) up to more than 60% conversion. Moreover, the corresponding M_n vs. conversion (%) plot [Figure 1(b)] although increases linearly with conversion up to 67%, the corresponding PDI initially remained almost constant up to about 20% conversion and then increases gradually with further increase in conversion. These results indicate the possible two steps pseudo first order polymerization reactions involving initial (a) slow solution phase polymerization followed by (b) faster solid phase polymerization. Consequently, the higher/faster chain-transfer reactions in solid phase polymerization are responsible for the gradual increase of PDI with conversion.

It is to be noted here that the observed molecular weights drifted gradually from the corresponding theoretical values with increase in conversion [Figure 1(b)]. Figure 2 shows the corresponding gradual peak shifting of the GPC chromatograms. All these results indicate that the propagating radical species concentration decreases slowly 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

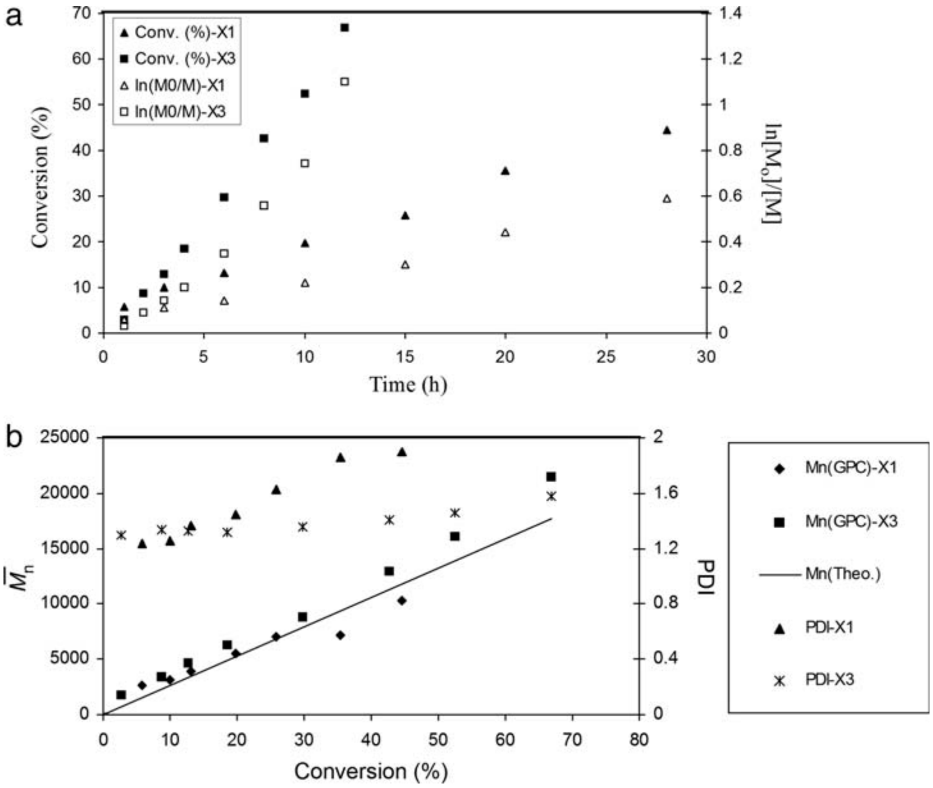


Figure 1. (a) Plots of time vs. monomer conversion and $\ln[M_o]/[M]$ (where $[M_o]$ = concentration of the monomer at time $t = 0$ min and $[M]$ = concentration of the monomer at the corresponding time) and (b) Plots of number-average molecular weight (M_n) and polydispersity (PDI) vs. monomer conversion in the bulk polymerization of *N*-vinylpyrrolidone (NVP) using [NVP] = 56.1 mmol, [X] = 0.28 mmol and [AIBN] = 0.057 mmol at 60°C.

transfer reactions to monomer/polymer or, to alkyne group at polymer chain end. Similar type of results are also reported in the literature.[9,15] It is to be noted here that GPC chromatogram of polymer obtained after 12 h has shoulder at higher molecular part (not shown here). This result indicates evidently the side reactions involving the loss of xanthate moieties from the polymer chain-end and supports the observed higher PDI values of the resulting polymers obtained after longer polymerization time.

To compare the rate of NVP polymerization using X_3 with respect to that of X_1,[15] the corresponding results obtained under the similar experimental conditions are also included in Figure 1. It is clear from the figure that the rate of pseudo-1st order polymerization reaction using X_3 (assuming overall linear polymerization rate) is almost 4.8 times faster with respect to that of X_1. Moreover, linear relationship is observed for X_1 up to only 45% conversion. Further, although the M_n increases linearly with conversion, the corresponding PDI increases gradually but considerably with conversion up to 45%. All these results indicate that X_3 is superior to X_1 in controlling polymerization of NVP under the experimental conditions. In this regard, comparative results of X_2 and X_4 are not included as they showed slow reactivity and poor control in NVP polymerization.

End-Group Analysis of Poly(NVP) Prepared Using X_3 RAFT Agent

Figure 3 shows ^{1}H-NMR (300 MHz, D_2O)) spectrum of poly (NVP) homopolymer [M_n (GPC) = 2300 g mol^{-1} and PDI = 1.25] obtained by the bulk polymerization of NVP using [NVP] : [X_3] : [AIBN] = 200 : 1 : 0.2 at 60°C for 45 min. Peaks from "e" to "j" are the characteristic repeating unit of the NVP as assigned in the figure. Rest peaks are coming from the X_3 RAFT agent. All 2-(propynyl propionate) protons except methine proton "c" are observed at around 1.2, 2.7, and 4.3 ppm,

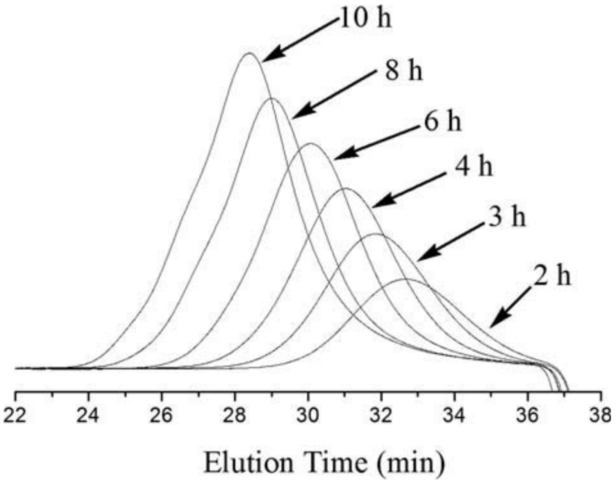


Figure 2. Gradual shifting of the gel permeation chromatograms in the kinetic study of the bulk polymerization of *N*-vinylpyrrolidone (NVP) using [NVP] = 56.1 mmol, [X_3] = 0.28 mmol and [AIBN] = 0.057 mmol at 60°C.

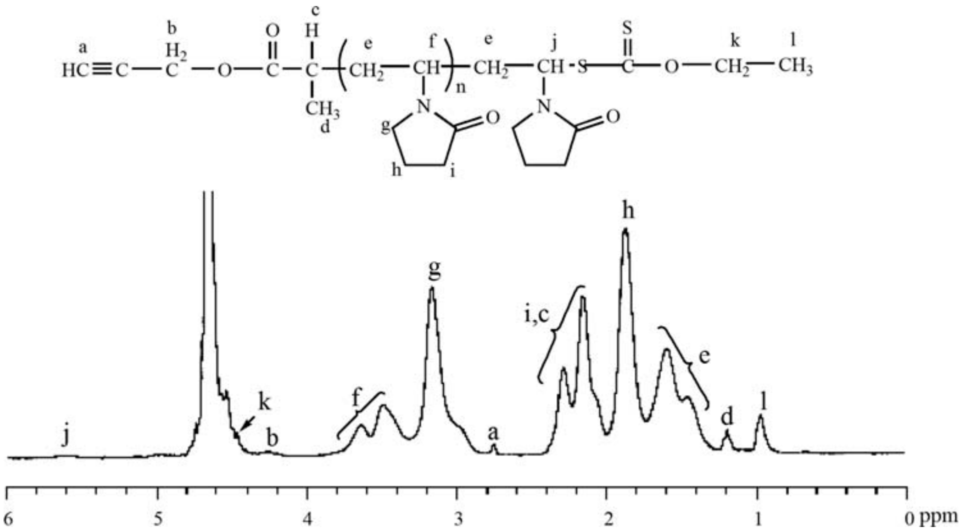


Figure 3. ^{1}H-NMR (300 MHz, D_2O)) spectrum of poly(NVP) macro-RAFT agent [M_n (GPC) = 2300 g mol^{-1} and PDI = 1.25] obtained by the bulk polymerization of NVP using [NVP]:[X_3]:[AIBN] = 200:1:0.2 at 60°C for 3 h.

respectively. Methine proton "c" of 2-(propynyl propionate) is overlapped on the peak of the methylene protons "i" adjacent to the keto group of the repeating unit. In addition, *O*-ethyl protons are observed at 0.97 and 4.5 ppm, respectively. The peak of the methine proton "j" of the terminal NVP group close to *O*-ethyl xanthate 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 "l". The corresponding M_n (NMR) was 1857 g mol^{-1}, which is close to the value (2300 g mol^{-1}) obtained by GPC measurement calibrated against PMMA standard. This indicates the formation of single chain from one molecule of xanthate mediator. In this regard, it is to be noted here that the peak ratio of "l" to "d" is 2.63. This indicates that the formed PNVP polymer contains 40% alkyne moiety at α-chain-end with respect to xanthate moiety at ω-chain-end. This observed low concentration of alkyne chain-end may be due to the loss of alkyne proton owing to its chain transfer reaction towards any radical or, due to the concomitant formation of AIBN-derived isobutyronitrile radical initiated PNVP polymer.

Figure 4 shows the FTIR spectra of (a) *O*-Propynyl-2-bromopropionate, (b) X_3 RAFT agent and (c) the above-mentioned alkyne-terminated PNVP macro-RAFT agent. In all spectra, the band at 2850-2940 cm^{-1} corresponds to both symmetric and asymmetric C—H stretching vibrations. A sharp single stretching vibration of carbonyl (C=O) bond of the ester is observed at around 1740 cm^{-1} in the spectra of (a) and (b). But the same is observed as a shoulder in the spectrum of alkyne-terminated PNVP; in addition to this, another single stretching vibration of carbonyl (C=O) bond of pyrrolidone group is observed at around 1658 cm^{-1}. The band due to terminal alkyne (C≡C—H) bond appears at around 3300 cm^{-1}; but the same is observed as a shoulder in the spectrum of alkyne-terminated

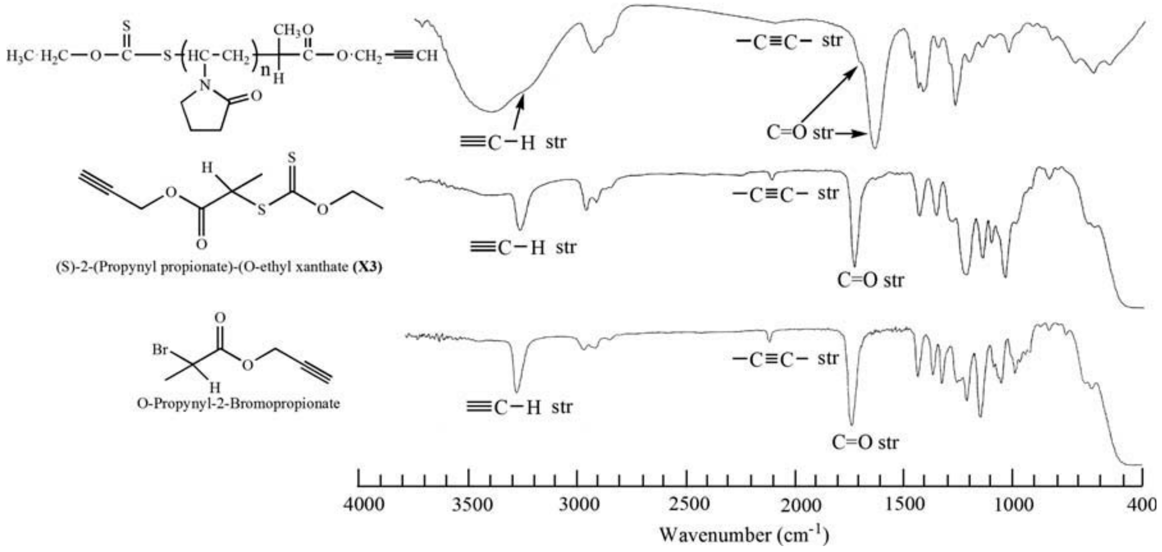


Figure 4. FTIR spectra of (a) *O*-Propynyl-2-bromopropionate, (b) X_3 RAFT agent, and (c) alkyne-terminated poly(NVP) macro-RAFT agent.

Table II. Chain-extension Experiment by RAFT Polymerization[a]

Run	Monomer (equiv.)	Macroinitiator[b] (Mn/PDI) (equiv.) against PMMA/ PSt Standard	Time (h)	Yield (%)[e] (Grav.)	Conv % (NMR)[f]	Final Polymer (M_n/PDI(GPC))[c] against PMMA/ PSt Standard	X_{PNVP} (NMR)[g]	X_{PNVP} (GPC)[g]
1	NVP(100)	(2300/1.25)[c]/(8000/1.14)[d] (1)	24	35.3	-	(7000/2.57)[c]/-	-	-
2	Styrene(100)	(2300/1.25)[c]/(8000/1.14)[d] (1)	24	-	43	(2800/1.27)[c]/(8200/1.23)[d]	0.93	0.82

[a]Using 0.2 equivalent AIBN in 0.5 mL DMF at 60°C, [b]Macroinitiator used was PNVP-X, [c]Determined by GPC(DMF, 0.5 mL/min, 40°C) calibrated against PMMA standard, [d]Determined by GPC(DMF, 0.5 mL/min, 40°C) calibrated against PStyrene standard, [e]Yield was determined gravimetrically, [f]Convesion was determined by ^{1}H NMR, [g]X_{PNVP} = mol-fraction of PNVP.

PNVP. The band at around 2130 cm^{-1} is due to triple bond (C≡C). Thus, the presence of the bands due to C═O, C≡C—H, and C≡C bonds confirms the presence of alkyne-terminated moiety at the chain-end of macro-RAFT agent.

CHAIN EXTENSION EXPERIMENTS BY RAFT POLYMERIZATION

Results of the homo and hetero chain extension experiments of alkyne-terminated PNVP macro-RAFT agent using RAFT polymerization method are shown in Table II.

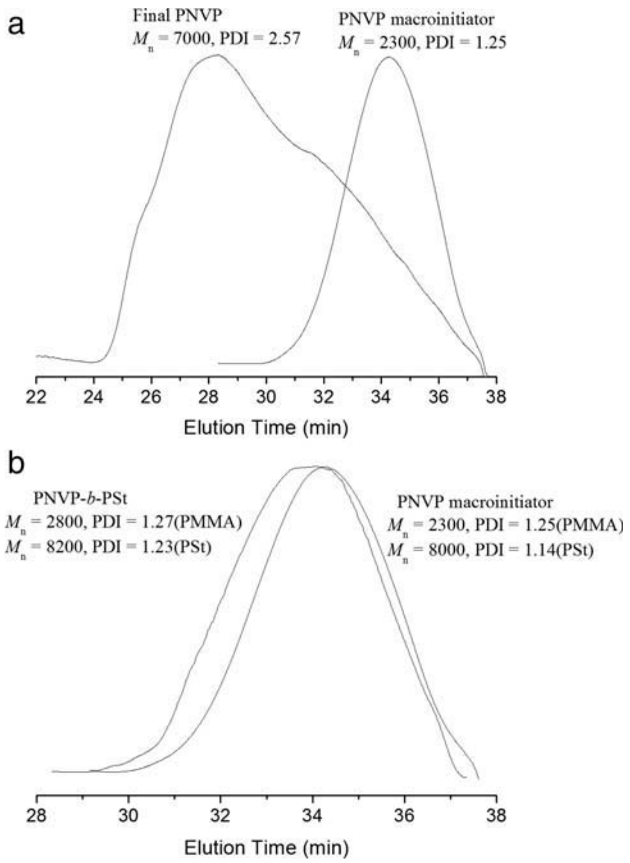


Figure 5. (a) Gel permeation chromatograms of PNVP macro-RAFT agent and final PNVP homopolymer in the homo-chain extension experiment. (b) Gel permeation chromatograms of PNVP macro-RAFT agent and the resulting poly(*N*-vinylpyrrolidone)-*b*-polystyrene in the hetero-chain extension experiment by RAFT method.

Homo-chain-extension experiment has been performed in DMF using [NVP] : [PNVP macro-RAFT agent] : [AIBN] = 100 : 1 : 0.2 at 60°C for 24 h. The observed monomer conversion was 35%. The corresponding GPC chromatograms for homo-chain extension experiment [Figure 5(a)] clearly show the shifting of the GPC chromatograms towards higher molecular weight. The presence of shoulder in this GPC chromatogram indicates a possible concomitant formation of AIBN-initiated PNVP homopolymers. The corresponding hetero chain extension experiment with styrene monomer has successfully been carried out in DMF using [St] : [PNVP macro-RAFT agent] : [AIBN] = 100 : 1 : 0.2 at 60°C for 24 h with 43% monomer conversion (Run 2, Table II). Figure 5(b) shows the corresponding GPC chromatograms. It is clearly showing the little shifting of the GPC chromatogram towards higher molecular weight. Moreover, the ^{1}H-NMR of this block copolymer (Figure 6) in $CDCl_3$ solvent shows clearly, in addition to the characteristic peaks of the PNVP 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. The observed mole fractions of PNVP block in this block copolymer are 0.82 calculated on the basis of M_n(GPC) values and 0.93 calculated on the basis of its ^{1}H-NMR (Table II). The observed higher value of PNVP fraction in the block copolymer from ^{1}H-NMR measurement indicates the presence of PNVP homopolymer as impurities. Therefore, the successful occurrence of these chain extension experiments support the living nature of the NVP polymerization using X_3 mediator. Similar type of results has also been reported in the literature.[9,15]

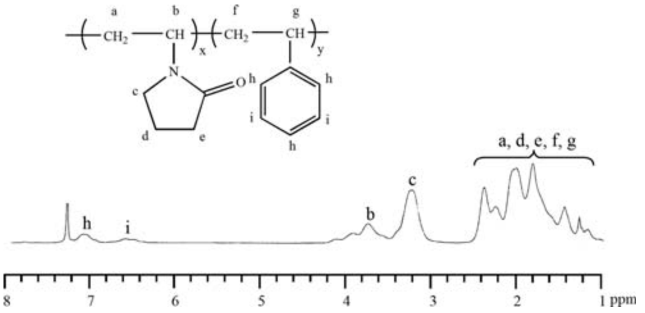


Figure 6. ^{1}H-NMR (300 MHz, $CDCl_3$)) spectrum poly(*N*-vinylpyrrolidone)-*b*-polystyrene obtained in the hetero-chain extension experiment by RAFT method using [St] : [poly(NVP) macro-RAFT agent] : [AIBN] = 100: 1 : 0.2 at 60°C for 24 h.

Table III. Chain-Extension Experiment by Click Chemistry^{a}

Run	Alkyne-terminated poly(NVP) macroinitiator (Mn/PDI) (equiv.) against PMMA/ PSt Standard	Azide-terminated poly(Styrene) macroinitiator (Mn/PDI) (equiv.) against PMMA/ PSt Standard	Yield (%)^{e}	Final Polymer (M_n/PDI(GPC)c against PMMA/ PSt Standard	X_{PNVP} (NMR)^{d}	X_{PNVP} (GPC)^{d}	cmc (mg/ mL)
1	(2300/1.25)^{b}/(8000/1.14)^{c} (1)	(2900/1.13)^{b}/ (10100/1.07)^{c} (1)	43	(3700/1.40)^{b}/(13000/1.18)^{c}	0.161	0.174	0.035
2	(2300/1.25)^{b}/ (8000/1.14)^{c} (1)	(5600/1.13)^{b}/ (16700/1.07)^{c} (1)	34	(6400/1.29)^{b}/(18900/1.16)^{c}	0.100	0.112	0.029

^{a}Using 1 equivalent CuBr in 0.5 mL DMF at 60°C, ^{b}Determined by GPC(DMF, 0.5 mL/min, 40°C) and calibrated against PMMA standard, ^{c}Determined by GPC(DMF, 0.5 mL/min, 40°C) and calibrated against polyStyrene standard, $^{d}X_{PNVP}$ = mol-fraction of PNVP, ^{e}Determined gravimetrically.

CHAIN EXTENSION EXPERIMENTS BY CLICK CHEMISTRY

The results of the hetero chain extension experiments through click chemistry using the same alkyne-terminated PNVP macro-RAFT agent and two azide-terminated polystyrene macro-initiators in DMF with [azide-terminated polystyrene] : [PNVP macro-RAFT agent] : [CuBr] = 1 : 1 : 1 at 80°C for 24 h are shown in Table III (Runs 1 and 2).

The yield of the resulting block copolymers are within 34–43%. Figure 7 shows the corresponding GPC chromatograms with the corresponding M_n(GPC) and PDI values calculated against both PMMA and PSt standards. It is clearly showing the shifting of the GPC chromatograms towards high molecular weight. Moreover, the typical ^{1}H-NMR spectrum of the block copolymer prepared at Run 1 in $CDCl_3$ solvent (Figure 8) shows clearly, in addition to the characteristic peaks of PNVP 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. In addition to these peaks, there is a peak at around 7.59 ppm due to the triazole ring proton. This also supports the formation of the block copolymer of NVP and styrene through click chemistry. The observed mole fractions of PNVP block (X_{PNVP}) in this block copolymer are 0.17 calculated on the basis of M_n(GPC) values and 0.16 calculated on the basis of ^{1}H-NMR

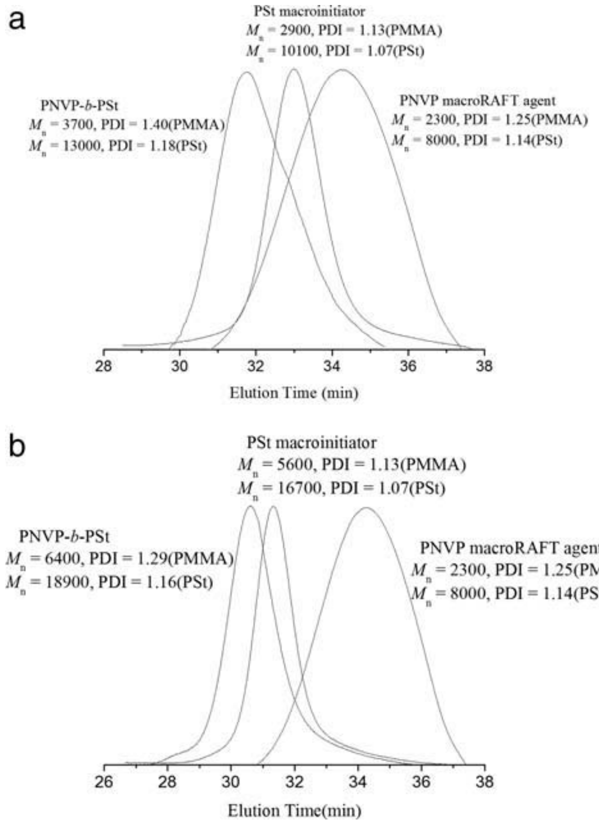


Figure 7. Gel permeation chromatograms of alkyne-terminated PNVP macro-RAFT agent, azide-terminated polystyrene and the resulting PNVP-*b*-PSt in the hetero-chain extension experiment by Click Chemistry: (a) Run 1, (b) Run 2. (Table III)

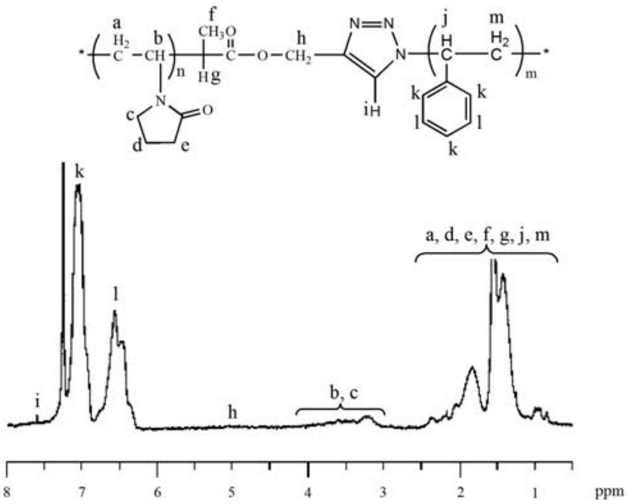


Figure 8. ^{1}H-NMR (300 MHz, $CDCl_3$)) spectrum poly(*N*-vinylpyrrolidone)-*b*-polystyrene obtained in the hetero-chain extension experiment by Click Chemistry (Run 1, Table III).

of this block copolymer. The observed X_{PNVP} in the block copolymer prepared in Run 2 are 0.11 calculated on the basis of M_n(GPC) and 0.100 calculated on the basis of its ^{1}H-NMR. All these results confirm the formation of the block copolymers of NVP and styrene through click chemistry. To study the amphiphilicity of such block copolymers, we have also measured the corresponding cmc values (Runs 1 and 2, Table III) in water by fluorescence spectroscopy using pyrene as probe. The corresponding semilogarithmic plots of the fluorescence excitation intensity ratio ($I_{337.07}/I_{333.07}$) of pyrene (6×10^{-7} *M*) (monitored at $\lambda_{em} = 394$ nm) vs. the concentration of the block copolymers are shown in Figure 9. The observed higher cmc value of the block copolymer of Run 1 is due to its shorter hydrophobic PSt block segment. Similar types of results were also reported in the literature.[22,23]

Thus, well-defined PNVP-*b*-PSt can be synthesized efficiently through click chemistry using alkyne-terminated PNVP and azide-terminated polystyrene.

Thermal Study

The thermal stabilities of the polymers were studied by using TGA. Figure 10 shows the TGA curves of polystyrene macroinitiator [M_n(GPC) = 10,100, PDI = 1.07], PNVP-macro-RAFT agent [M_n(GPC) = 2300, PDI = 1.25] and PNVP-*b*-PSt block copolymer (Run 1, Table III). The decomposition of PSt occurs through one-step degradation initiates at 340°C. On the other hand, PNVP has a higher thermal stability than PSt. PNVP undergoes initial slight weight loss at ~ 90–120°C owing to the evaporation of adsorbed moisture followed by broad mass loss in the region ~ 400–420°C due to the degradation of the back bone chain of PNVP.[24] Degradation thermogram of PNVP-*b*-PSt (Run 1, Table III) block copolymer is of the intermediate type having also single steps degradation initiated at ~ 340°C.

DSC thermograms of polystyrene macroinitiator [M_n(GPC) = 10,100, PDI = 1.07], PNVP-macro-RAFT agent [M_n(GPC) =

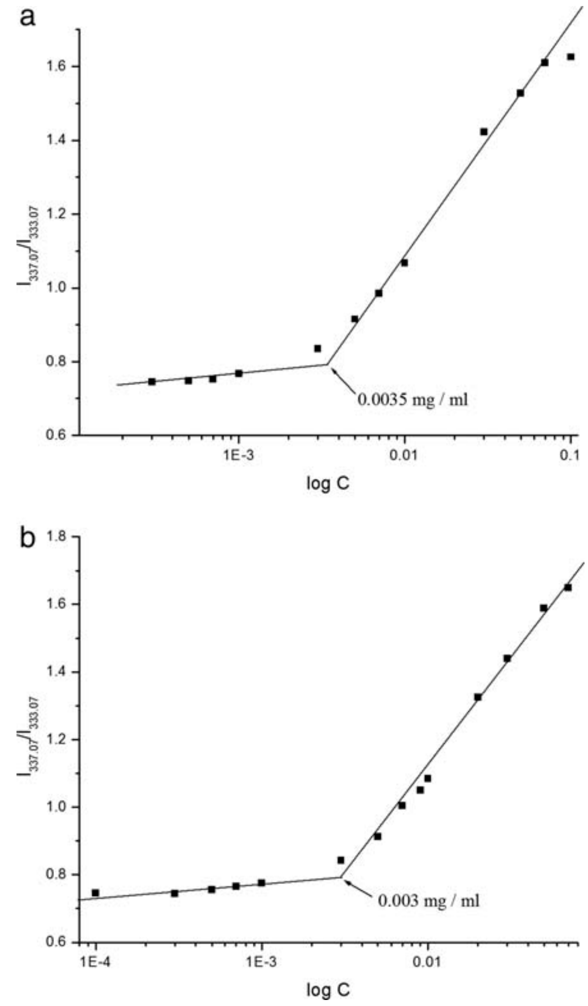


Figure 9. Semilogarithmic plot of the fluorescence excitation intensity ratio ($I_{337.07}/I_{333.07}$) of pyrene (6×10^{-7} *M*) (monitored at $\lambda_{em} = 394$ nm) vs. the concentration of poly(NVP)-*b*-polystyrene block copolymer of (a) Run 1 and (b) Run 2 (Table III) in water.

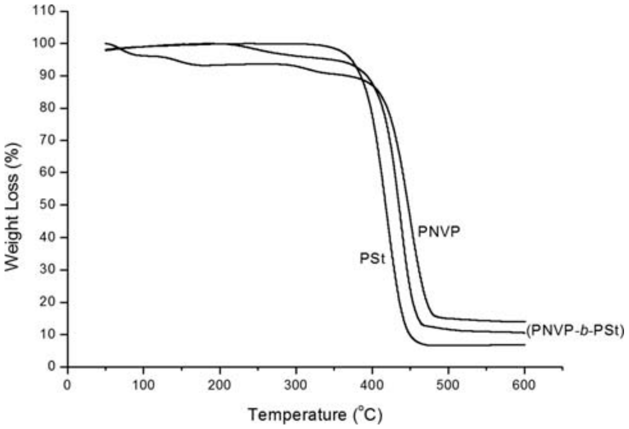


Figure 10. TGA thermograms of PNVP-macro-RAFT agent [M_n(GPC) = 2300, PDI = 1.25], PSt-macroinitiator [M_n(GPC) = 10,100, PDI = 1.07], and PNVP-*b*-PSt block copolymer (Run 1, Table III). Heating rate: 20°C/min under N_2.

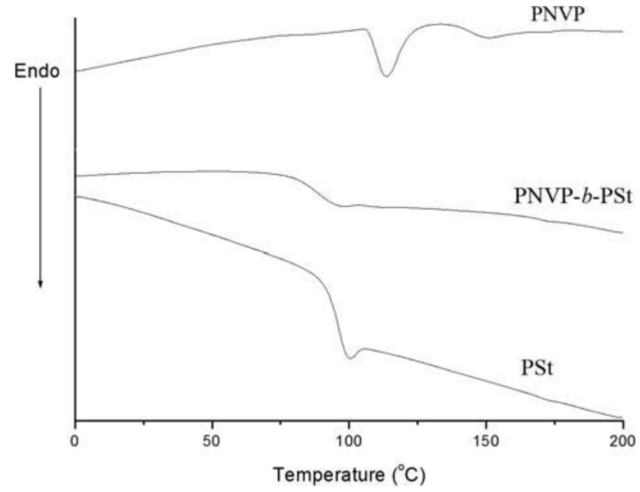


Figure 11. DSC thermograms of PNVP-macro-RAFT agent [M_n(GPC) = 2300, PDI = 1.25], PSt-macroinitiator [M_n(GPC) = 10,100, PDI = 1.07], and PNVP-*b*-PSt block copolymer (Run 1, Table III). Heating rate: 10°C/min under N_2.

2300, PDI = 1.25] and PNVP-*b*-PSt block copolymer (Run 1, Table III) are shown in Figure 11. In the second heating run, the glass transition temperature (T_g) of PSt-macroinitiator is observed at ~ 100°C. PNVP did not show any melting endotherm or exotherm.[25] The secondary transition temperature of its at 115°C is due to the relaxation of its pendent pyrrolidone group. The sharp secondary transition temperature at 155°C is due to the glass transition temperature (T_g) of the backbone chain of PNVP. The single glass transition temperatures (T_g) of PNVP-*b*-PSt (Run 1, Table III) is observed at 97°C. This observation of the single T_g peak of the block copolymers may be due to the miscibility of the PNVP micro-domain within the PSt macro-domain.

CONCLUSIONS

Two new alkyne-terminated xanthate RAFT agents: (*S*)-2-(propynyl propionate)-(*O*-ethyl xanthate) (X_3) and (*S*)-2-(propynyl isobutyrate)-(*O*-ethyl xanthate) (X_4) are synthesized and characterized and used for the controlled radical polymerization of NVP. X_3 shows better chain transfer ability in the polymerization at 60°C using [X_3]:[AIBN]::1:0.2. Molecular weight of the resulting polymer increases linearly with the increase in the monomer loading. Kinetics study with X_3 shows the psuedo-first order kinetics up to 67% monomer conversion. Molecular weight (M_n) of the resulting polymer increases linearly with the increase in the monomer conversion up to around 67%. With the increase in the monomer conversion, polydispersity of the corresponding PNVPs initially decreases from 1.34 to 1.32 and then increases gradually to 1.58. Chain-end analysis of the resulting polymer by ^{1}H-NMR and FTIR shows clearly that polymerization is started with radical forming out of xanthate RAFT agent. Living nature of the polymerization is also confirmed from the successful homo-chain extension experiment and the hetero-chain extension experiment involving synthesis of PNVP-*b*-polystyrene amphiphilic diblock copolymer. Formed alkyne-terminated poly(NVP) allows easy conjugation to azide-terminated polystyrene through click chemistry to prepare well-defined PNVP-*b*-polystyrene block copolymers. Resulting polymers are characterized by GPC, ^{1}H-NMR, FTIR, and thermal study.

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