RAFT Polymerization of *N*-Vinyl Pyrrolidone Using Prop-2-ynyl Morpholine-4-carbodithioate as a New Chain Transfer Agent

Vivek Mishra, Rajesh Kumar

Organic Polymer Laboratory, Department of Chemistry, Centre of Advanced Studies in Chemistry, Banaras Hindu University, Varanasi-221005, UP, India

ABSTRACT: RAFT polymerization of *N*-vinyl pyrrolidone (NVP) has been investigated in the presence of chain transfer agent (CTA), i.e., prop-2-ynyl morpholine-4-carbodithioate (PMDC). The influence of reaction parameters such as monomer concentration [NVP], molar ratio of [CTA]/[AIBN, i.e., 2,2'-azobis (2-methylpropionitrile)] and [NVP]/[CTA], and temperature have been studied with regard to time and conversion limit. This study evidences the parameters leading to an excellent control of molecular weight and molar mass dispersity. NVP has been polymerized by maintaining molar ratio [NVP]: [PMDC]: [AIBN] = 100 : 1 : 0.2. Kinetics of the reaction was strongly influenced by both temperature and [CTA]/[AIBN] ratio and to a lesser extent by monomer concentration. The activation energy (E_a = 31.02 kJ mol^{-1}) and enthalpy of activation ($\Delta H^{\ddagger}$ = 28.29 kJ mol^{-1}) was in a good agreement to each other. The negative entropy of activation ($\Delta S^{\ddagger}$ = −210.16 J mol^{-1}K^{-1}) shows that the movement of reactants are highly restricted at transition state during polymerization. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4475–4485, 2012

Key words: living polymerization; dithiocarbamate; *N*-vinyl pyrrolidone; activation energy

INTRODUCTION

The thiocarbonylthio moieties have been found effective in controlling the polymerization by reversible addition-fragmentation chain transfer (RAFT)[1,2] process. There have been a number of publications ever since, clearly indicating the versatility of the RAFT systems using various monomers in both homogeneous and heterogeneous environments. A book by Chiefari and Rizzardo on radical polymerization comprises a chapter, which deals with the work done in the RAFT area.[3] RAFT agents (also called chain-transfer agents) must be thiocarbonylthio compounds where the Z and R groups perform different functions. The Z group primarily controls the ease with which radical species add to the C=S bond. The R group plays an important role—it must be a good homolytic leaving group which is able to initiate new polymer chains. There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the activating (Z) group: (i) dithioesters (Z = aryl or alkyl), (ii) trithiocarbonates (Z = substituted sulfur), (iii) dithiocarbonates (xanthates, i.e., ROC(=S)SR') and (iv) dithiocarbamates (Z = substituted nitrogen). The combination that would be the best suited for specific monomers has been also found.

In a RAFT mechanism, initiation occurs via the decomposition of the free radical initiator leading to formation of propagating chains. This is followed by addition of the propagating radical to the RAFT agent. Further, the fragmentation of the intermediate radical occurs, giving rise to a polymeric RAFT agent and new radical. This radical reinitiates the polymerization to form new propagating radicals. The RAFT process relies on this rapid central addition fragmentation equilibrium between propagating and intermediate radicals, and chain activity and dormancy as shown in Scheme 1.[4]

Before the invention of controlled radical polymerization, the vinyl monomers were polymerized through conventional (redox) free radical polymerization process to prepare copolymers[5,6] and homopolymers. Conventional free radical polymerization has some drawbacks such as high molar mass dispersity, formation of side products, and uncontrollability of reaction. Controlled/living radical polymerization methods[7,8,10–20] has been explored widely for the controlled synthesis of homopolymers and block copolymers. Rizzardo et al.[7] reported first in a patent about reversible addition-fragmentation chain transfer (RAFT) polymerization of NVP. Later,
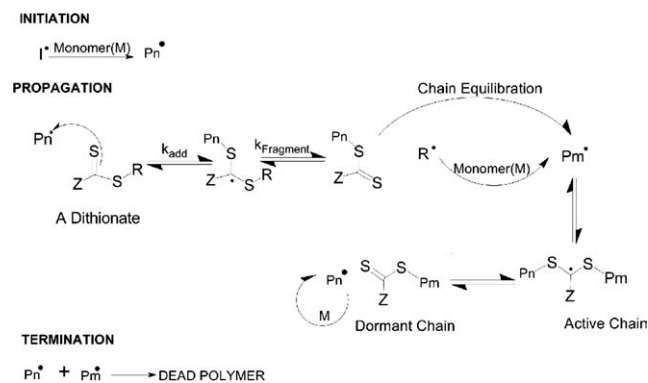
Scheme 1 RAFT equilibrium during polymerization process.

Matyzaszewski et al.[8] reported the synthesis of low molecular weight and low molar mass dispersity (M_n = 2000, Đm[9] = 1.15) poly(NVP) using copper-catalyzed atom transfer radical polymerization (ATRP). In both reports, details have not been disclosed. Using xanthate-type RAFT agent, Kamigaito et al.[10] reported the controlled radical polymerization of NVP as well as the simultaneous control of molecular weight of poly(NVP) by performing polymerization in fluoroalcohols. Gnanou et al.[11] also reported the controlled radical polymerization of NVP using dithiocarbamate-type RAFT agents. Hadjichristidis et al.[12] also reported the controlled radical polymerization of NVP using nitroxide-mediated and RAFT polymerization methods. However, they did not report so far the detailed study of the RAFT polymerization of NVP.

NVP is neither a skin sensitizer nor a primary irritant. Generally, N-vinyl-2-pyrrlidone imparts desirable properties when as little as 1.20% is polymerized with another monomer or monomer grafted on the polymeric backbone. Incorporation of high molecular weight poly(N-vinyl pyrrolidone) increases the transparency of polyamides and improves dye receptivity of cellulose derivatives. Combination of cellulose and poly(N-vinyl pyrrolidone) is also used as hemodialysis membranes.[21,22] Its suspending ability is a chief reason for its wide use in pill tabelating, capsule granulation and in amitriptyline-25 tablet formulation on drug dissolution.[23] Poly(N-vinyl pyrrolidone) is used in the preparation of odor masking compound,[24] thus acting as odor neutralizer in aerosol deodorants to remove unpleasant odors of human and animal hair. NVP is also widely used in cosmetics,[25] textiles,[26] and pharmaceuticals.[27]

Present investigation was undertaken to study in detail the living and controlled polymerization of N-vinyl pyrrolidone with narrow molar mass dispersity, which can have better applications than the polymer formed by uncontrolled polymerization process. This prompted us to carry out the synthesis of new RAFT agent and their application in controlled radical polymerization of N-vinyl pyrrolidone by RAFT process. In the present work, synthesis of new chain transfer agent, i.e., prop-2-ynyl morpholine-4-carbodithioate, characterization and optimization of reaction conditions of polymerization process to get narrow molar mass dispersity of poly (N-vinyl pyrrolidone) which could have better application than the polymer formed by uncontrolled polymerization process and kinetics of controlled process in detail is being reported.

EXPERIMENTAL

Materials

Morpholine (99%, Merck) has been stored over metallic sodium under N_2 atmosphere for 24 h and finally distilled under reduced pressure. 2, 2′-Azobis (2-methylpropionitrile) (AIBN) (Fluka, 98%) has been purified by recrystallization from ethanol. Tetrahydrofuran (THF; 99.8%, Merck) has been dried and distilled over benzophenone and sodium. Propargyl bromide (80 wt% in toluene, Aldrich), dry dimethyl formamide (DMF; 99.8%, Merck), N-vinyl pyrrolidone (NVP; 99%, Aldrich), carbon disulfide (CS_2), sodium hydroxide (NaOH) have been used as received. Other solvents have been purified by conventional procedures.

All the reaction parameters have been calculated by following formulae:

$$\text{Conversion}_{\text{NMR}} = \frac{A_{\text{Polymer}}}{A_{\text{Polymer}} + A_{\text{Monomer}}} \quad (1)$$

All the monomer conversion for the kinetic study have been estimated by ¹H NMR with the samples directly withdrawn at time intervals, the monomer conversion being estimated by comparing the peak areas of the monomer and homopolymer. The exact monomer conversion and M_n NMR of polymers can be calculated using eqs. 1 and 2.

$$M_{n(\text{NMR})} = M_{\text{PMDC}} + M_{\text{NVP}} \times \frac{[\text{NVP}]_0}{[\text{PMDC}]_0} \times \text{Conversion}_{\text{NVP}} \quad (2)$$

The theoretical number-average molecular weight on conversion is defined as follows:

$$M_{n\,(\text{THEO})} = \frac{[\text{NVP}]_0}{[\text{PMDC}]_0 + 2f[\text{I}]_0(1 - e^{-k_d t})} \times M_{\text{NVP}} \times \text{Conversion}_{(\text{NVP})} + M_{\text{PMDC}} \quad (3)$$

in which M_{PMDC} and M_{NVP} are molecular weights of chain transfer agent and the monomer, whereas

$[NVP]_0$ and $[PMDC]_0$ are the initial concentrations of the monomer and chain transfer agent, respectively. The right-hand side of the denominator accounts for radicals derived from initiator with an initial concentration $[I]_0$ at time t with a decomposition rate, k_d. The initiator efficiency is represented by f. In an ideal RAFT process, polymer directly derived from the initiators is minimal, and thus the second term in the denominator becomes negligible[28–30] and eq. 3 can be simplified to eq. 4.

$$M_{n(\text{theo})} = \frac{[NVP]_0}{[PMDC]_0} \times M_{\text{NVP}}$$
$$\times \text{Conversion}_{(\text{NVP})} + M_{\text{PMDC}} \quad (4)$$

$$M_{n(\text{UV})} = \frac{w}{c_{\text{PMDC}}} \quad (5)$$

where w is the weight of polymer[31] sample analyzed (in g), C_{PMDC} is the amount of PMDC residues in the polymer sample (in mol) determined experimentally by application of Beer's law and using the molar extinction coefficient of PMDC. The absorbance of polymer was recorded and the concentration of PMDC was calculated using the molar extinction coefficient of PMDC determined above.

$$\text{Initiator efficiency } (f) = M_{n(\text{THEO})}/M_{n(\text{GPC})} \quad (6)$$

$$\text{Degree of Polymerization (DP}_n) = \frac{[NVP]_0}{[PMDC]_0}$$
$$\times \text{Conversion}_{(\text{NVP})} \quad (7)$$

It is a well-known fact that raising the temperature increases the reaction rate, though, quantitatively, activation energy and frequency factor are determined by the Arrhenius eq. 8:

$$k = A.e^{-\frac{E_a}{RT}} \quad (8)$$

where E_a = activation energy, R = 8.314 [J mol $^{-1}$K^{-1}], T = absolute temperature in K, A = frequency factor, $A = pZ$, where Z is the collision rate and p is a steric factor. Z turns out to be only weakly dependant on temperature. Thus, the frequency factor is a constant, specific for each reaction.

The Eyring equation is calculated from eq. 9:
The linear form of the Eyring equation is

$$\ln \frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \quad (9)$$

where k_B = Boltzmann's constant [1.381 $\times$ 10^{-23} JK^{-1}], T = absolute temperature in K, h = Plank constant [6.626 $\times$ 10^{-34} J s].

A plot of $\ln(k/T)$ versus $1/T$ produces a straight line then $y = -mx + b$, where $(x = 1/T)$. Activation of enthalpy $(\Delta H^{\ddagger})$ can be calculated from the slope m of this line: $\Delta H^{\ddagger} = -m R$.

From the y-intercept,

$$y(x = 0) = \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \quad (10)$$

Activation of entropy $(\Delta S^{\ddagger})$ can be determined and thus the calculation of $\Delta G^{\ddagger}$ for the appropriate reaction temperatures according to eq. 11 is allowed.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger} \quad (11)$$

where R = universal gas constant = 8.3145 [J mol^{-1} K^{-1}], $\Delta G^{\ddagger}$ = free activation enthalpy [kJ mol^{-1}], $\Delta S^{\ddagger}$ = activation entropy [J mol^{-1}K^{-1}], $\Delta H^{\ddagger}$ = activation enthalpy [kJ mol^{-1}].

Techniques of characterization

^{1}H NMR spectra were recorded on a JEOL AL300 NMR spectrometer at 25°C in CDCl$_3$ as solvent at 300 MHz and are reported in parts per million (ppm) from internal tetramethylsilane. FTIR spectra of the samples were recorded by making pellets in KBr and in neat using Varian Excalibur 3100 spectrometer (Palo Alto, CA) in the 400 cm^{-1} to 4000 cm^{-1} region with 4 cm^{-1} resolution and 32 scans. UV–vis spectra were recorded on PerkinElmer–Lambda 35 UV-vis Spectrophotometer at 25°C. The optical path length of measurement cell was 10 mm. The number average molecular weight (M_n) and molar mass dispersity (Đm) 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 lm 10E 4Å 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 poly(methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10).

Synthesis of prop-2-ynyl morpholine-4-carbodithioate: A RAFT agent

Morpholine (17.40 g, 0.20 mol) and methanol (20 mL) were added into a 100-mL Erlenmeyer flask and the solution was cooled to 0°C in an ice bath (Scheme 2). Carbon disulfide (7.60 g, 0.10 mol) was added dropwise through a pressure equalizing dropping funnel over 30 min with vigorous stirring, then a solution of NaOH (4 g, 0.10 mol) in 20 mL methanol was added and the mixture was stirred at 60°C for 1 h under high purity nitrogen and stirred until the NaOH was completely dissolved. About three-quarters of the methanol were removed using a
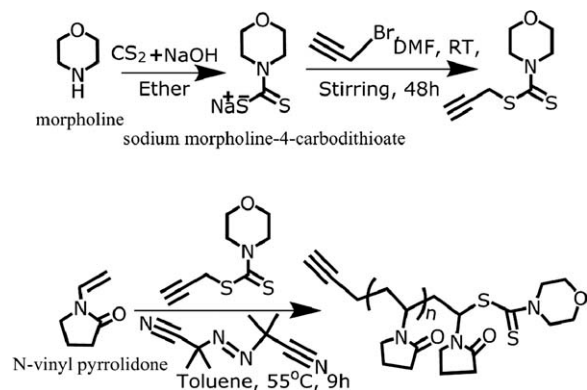
Scheme 2 Experimental conditions for RAFT polymerization process for NVP.

rotavapor. The mixture was chilled and poured into 40 mL of diethyl ether. The white precipitate (sodium salt of morpholine dithiocarbamic acid $(MDC^- Na^+)$) was filtered and dried at 40°C for 2 h under vacuum. This precipitate was dissolved into 10 mL of dry toluene. Propargyl bromide (11.8 g/15.75 mL, 0.1 mol) was added slowly to this reaction mixture of sodium salt of morpholine dithiocarbamic acid. The reaction mixture was degassed by three freeze pump thaw cycles and left *in vacuo*. The mixture was allowed to stir overnight. The solution was extracted with diethyl ether and then solvent was removed under reduced pressure to get clear yellow liquid (scheme 2). ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.861 (s, 2H, —CH^b), 3.257–3.384 (dd, 8H, —C$H^{c,d}$), 2.275 (s, 1H, CH^a) (Fig. 1). FT-IR (Neat, cm^{-1}): 3294, 3008, 2961, 2633, 2123, 1717, 1619, 1515, 1422, 1291, 1256, 1211, 1148, 1108, 1028, 958, 872, 804 (Fig. 3). UV (in DMSO): 271 and 295 nm (Fig. 4, curve B).
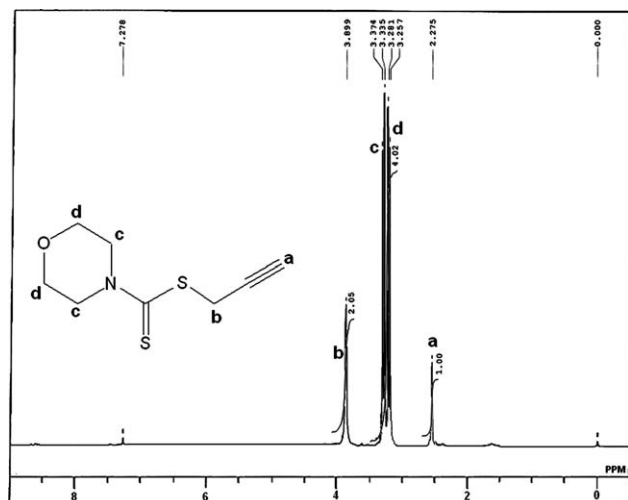
Prop-2-ynyl morpholine-4-carbodithioate mediated RAFT polymerization of NVP and its purification

Eleven milliliters (100 mmol) of distilled *N*-vinyl pyrrolidone (NVP), AIBN initiator (32.8 mg, 0.2 mmol), and chain transfer agent (PMDC; 201 mg, 1 mmol) were placed in a dry Schlenk tube equipped with a magnetic stirring bar, and then the solution was degassed by three freeze-evacuate-thaw cycles. The flask was immersed in a preheated oil bath at 55°C for desired time. The color of the solution changed from colorless to yellow and to brown. After definite time intervals, a small portion of the reaction mixture was taken out to determine the monomer conversion by ^{1}H NMR. Rapid cooling with liquid nitrogen stopped the reaction. For the determination of the monomer conversion, polymer was precipitated in hexane. For purification of polymer, precipitate was dissolved in minimum amount of DMF and reprecipitated into excess of hexane. The conversion determined by this method was 72%. The resulting polymer was soluble in methanol, CHCl$_3$, DMSO, DMF, and basic water. 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. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.990–4.886 (d, 1H, CH^i), 4.565–4.473 (t, 8H, C$H^{j,k}$), 3.489–3.326 (br, m, C$H^{d,g}$), 2.708 (s, 1H, CH^a), 2.389–2.275 (br, m, CH^e), 2.169–1.992 (m, br, C$H^{b,f}$), 1.308–1.132 (br, m, C$H^{c,h}$) (Fig. 2). FT-IR (KBr, cm^{-1}): 3600–3400 (ν$_{due to absorbed moisture}$), 3308(ν$_{\equiv CH str}$), 2979 (ν$_{CH str}$), 1696 (ν$_{N—CO—, str. for cyclic tertiary amide}$), 1514, 1426 (ν$_{C—N str.}$), 1361(ν$_{C—O, bending, med}$), 1256, 1196, 1097 (ν$_{C—C—C bending, medium}$), 1086 (ν$_{C=S str}$), 1083 (ν$_{C—S str}$), 1008 (ν$_{C—C str., weak}$), 832 (ν$_{C—H bending of the ring , medium}$), 649 (ν$_{C—S str}$) (Fig. 3). UV (DMSO): 270 and 292 nm (Fig. 4, curve C).

Figure 1 ^{1}H NMR spectra of prop-2-ynyl morpholine-4-carbodithioate (PMDC).
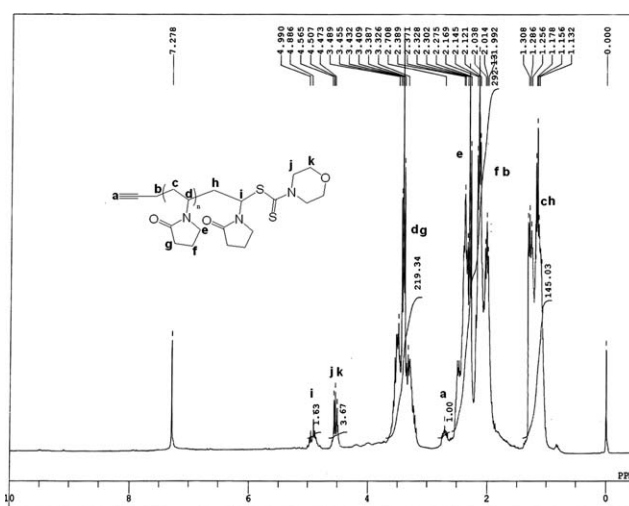

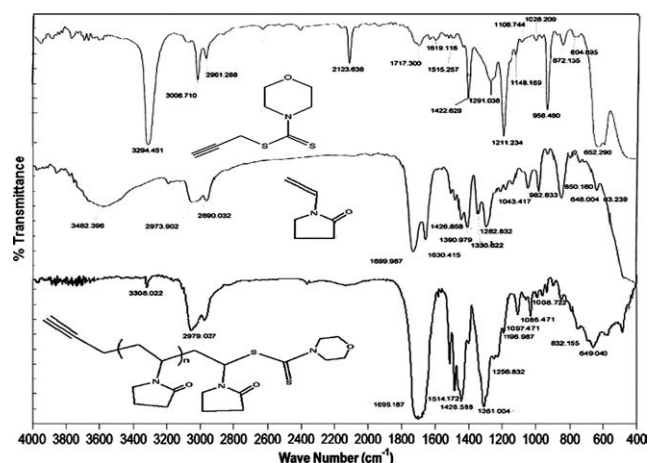**Figure 2** ^{1}H NMR spectra of PMDC_NVP polymer

Figure 3 IR spectra of prop-2-ynyl morpholine-4-carbodithioate (PMDC) and its polymer PMDC_NVP.

Polymer synthesis and characterization

The protocol used for the RAFT synthesis of a linear poly (N-vinyl pyrrolidone) homopolymer was as follows: PMDC RAFT agent (201 mg, 1 mmol) and NVP monomer (11 mL; 100 mmol) were added into a 100 mL Schlenk flask, degassed using three freeze-pump-thaw cycles and refilled with nitrogen for 30 min. Anhydrous toluene (11 mL, 80 wt%) was added *via* a N_2-purged glass syringe and the mixture was purged with nitrogen for 10 min. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 32.8 mg, 0.2 mmol, PMDC/AIBN molar ratio =5 : 1) was added at last under a positive pressure of nitrogen before the flask was immersed in a preheated oil bath at 55°C. This degassed stock solution was divided into eleven dry and degassed polymerization glass tubes. Aliquots (typically 0.20 mL) were periodically extracted for GPC and ^{1}HNMR analyses for conversion. In the latter case, spectra were recorded in $CDCl_3$ and the signals due to the residual vinyl protons of monomer at δ 4.31–4.42 (2H) ppm and δ 7.01 (1H) were compared with 3.489–3.326 ppm [(d) and (g) in Fig. 2] for the —NCH, and —NCOCH$_2$ of the corresponding polymer. After 9 h, the polymerization was terminated by exposure to air and cooling the reaction flask in liquid nitrogen. Toluene was removed under reduced pressure and polymer was precipitated in hexane. For purification of polymer, precipitate was dissolved in minimum amount of DMF and reprecipitated into excess of hexane to remove any unreacted monomer. The conversion of monomer to polymer was obtained 72%. Finally, the homopolymer was dried for 24 h in a vacuum oven at 50°C gave light pink powder. The molecular weight (M_n) and molar mass dispersity (Đm) of the obtained polymer were determined as 9430 and 1.15, respectively. PMDC will be examined as chain-transfer agent in the RAFT polymerization of NVP. The

signals at δ 4.565–4.473 ppm correspond to the ring protons of PMDC units. The appearance of the signals at 4.565–4.473 ppm indicates that the dithioester formed from PMDC reacted with primary or propagating radicals (Scheme 3 and Fig. 2), and that the PMDC moiety remained at the end of polymer chain. The appearance of cyclic tertiary amide at 1696 cm^{-1} for N—C=O; 1514, 1426 cm^{-1} for C—N stretching[32] and 1361 cm^{-1} for C—O bending of N-vinylpyrrolidone (Fig. 3). The band of PMDC RAFT agent appears at 1086 cm^{-1} for C=S stretching and 649 cm^{-1} for C—S stretching. These bands in FTIR spectra of polymer[33–37] support the successful RAFT polymerization of N-vinyl pyrrolidone (Fig. 3). UV analyses show the peak at 254 nm, which is due to the morpholine unit and two peaks at 271 and 290 nm for carbodithioate unit (Fig. 4, curve A). Figure 4 (curve B) shows two maxima in which band at 280 nm are due to propargyl group and other one at 257 nm is due to MDC. PMDC-NVP polymer shows three maxima on 256, 280, and 309 nm, i.e., due to the MDC, propargyl, and N-vinyl pyrrolidone units. The presence of these peaks in polymer supports the successful RAFT polymerization (Fig. 4, curve C).

RESULTS AND DISCUSSION

Kinetic studies

A linear relationship between $\ln[M]_0/[M]_t$ and reaction time is shown in Figure 5. The first-order kinetics indicates that the concentration of free radicals remained constant during the polymerization.[38–40] The plots of M_n and molar mass dispersity versus monomer conversion of NVP are shown in Figure 6. M_n values increased linearly with conversion, while the molar mass dispersity remained in a relative low value
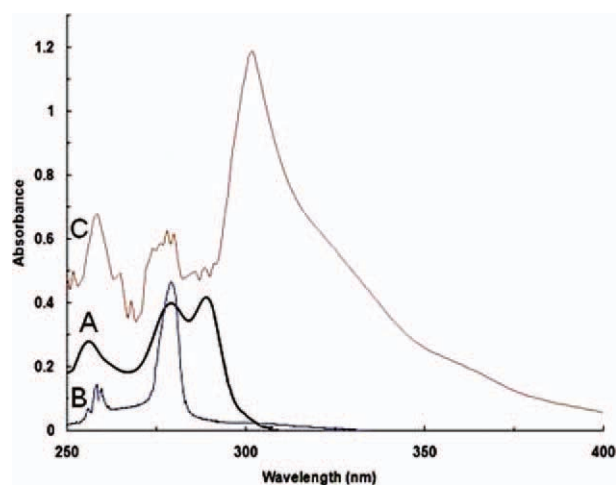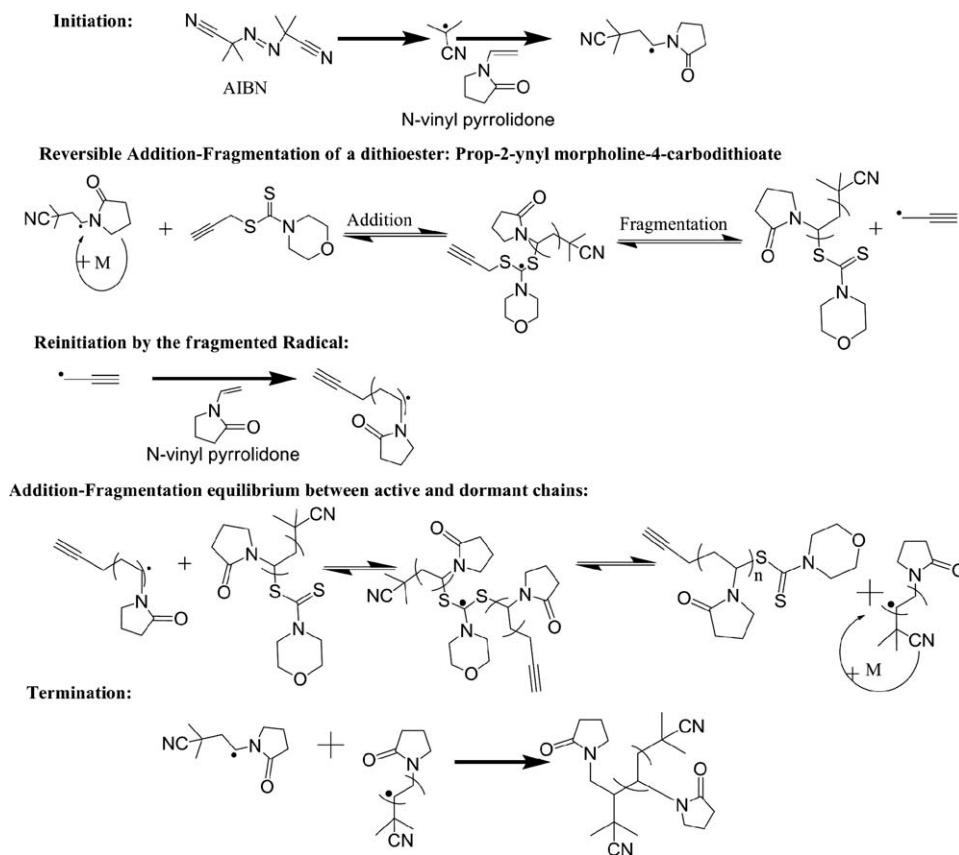

Figure 4 UV spectra of (a) morpholine-4-carbodithioate (MDC), (b) prop-2-ynyl morpholine-4-carbodithioate (PMDC) and (c) PMDC_NVP polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 3 RAFT mechanism in the presence of prop-2-ynyl morpholine-4-carbodithioate.

(1.50–1.15). These results suggest that PMDC is an effective RAFT agent for controlled the polymerization of NVP at the reported experimental conditions.

Living radical polymerization of NVP: Chain Extension of PNVP

To confirm further that the polymerization is a "living" process, a chain extension experiment was car-

ried out using obtained polymer as the macro-CTA using the molar ratio [NVP]: [Macro-CTA]: [AIBN] = 100 (1 mmol = 0.11 mL) : 1 (0.01 mmol $\approx$ 110 mg of M_n 9430) : 0.2 (0.01 mmol = 1.64 mg) in 20 mL of toluene. This mixture was placed in a reaction ampule. After three freeze-evacuate-thaw cycles, the polymerization mixture was stirred at 55°C for 12 h. The plot of the monomer $\ln([M]_o/[M_t])$ and (%)
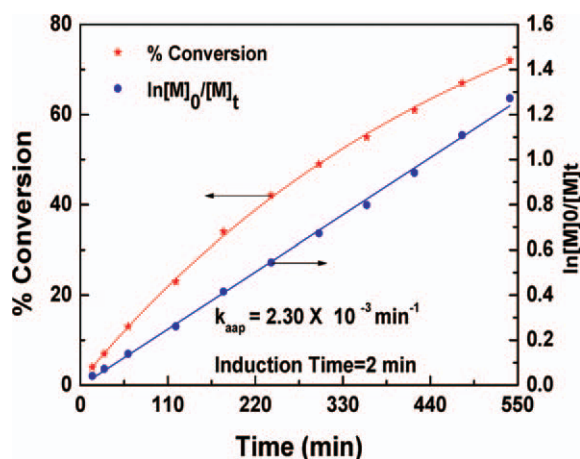

Figure 5 Kinetic plot to determine K_{aap} constant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
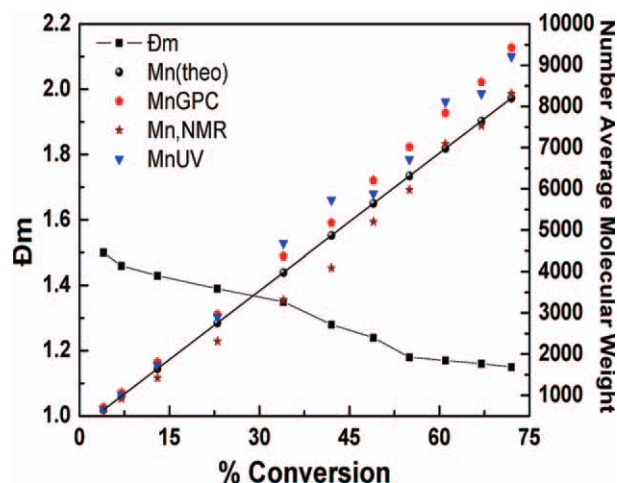

Figure 6 Main graph M_n vs % conversion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
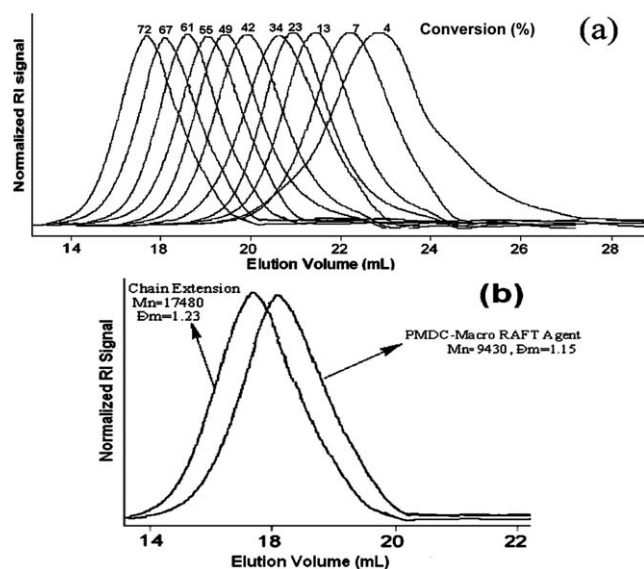
Figure 7 (a) Trace of GPC chromatograms of PMDC_NVP at different time (b) chain extension of NVP (52% conversion).

conversion versus time (Fig. 5) indicates that the monomer (%) conversion increases almost linearly upto around 52% conversion and followed the pseudo-first-order kinetics.[41,42] This behavior may be due to auto-acceleration (gel-effect) at higher monomer conversions. Molecular weight (M_n = 9430) increases linearly with (%) conversion upto 52% (M_n = 17,480) [Figs. 6 and 7(b)]. The observed molecular weights drifted gradually from the corresponding theoretical values with increase in conversion. The corresponding Đm increases gradually from 1.15 to 1.23 [Figs. 6 and 7(b)] with increase in (%) conversion, this broadening is due to the high viscosity of the medium. Figures 7(a,b) show the corresponding gradual peak shifting of the GPC chromatograms in the above-mentioned kinetic study. ^{1}H NMR spectrum shows the consistent growth of polymer chain as well as propargyl group of CTA is incorporated at α-end of the polymer chain, while ω-end remains with terminal morpholine dithiocarbamate. This successful chain extension and characterization of polymers suggests that the polymerization is a living process.

Mechanism of RAFT polymerization

RAFT is based on process that consists of the simple introduction of a small amount of PMDC (CTA) in a conventional free-radical system. The transfer of the PMDC between growing radical chains, present at a very low concentration, and dormant polymeric chains, present at a higher concentration, will regulate the growth of the molecular weight and limit the termination reactions. The mechanism of RAFT

polymerization, as it is generally accepted, is depicted in Scheme 1.

Initiation

Initiation occurs via the decomposition of the free radical initiator (AIBN). The radical species issued from the decomposition of the radical initiator reacts with the monomer (k_i) which starts an active polymerizing chain.

Reversible addition fragmentation

It shows that growing polymer chain rapidly adds to the reactive C=S bond of the PMDC (k_{add}) to form a radical intermediate (the radical initiator may add directly onto the PMDC, before reacting with any monomer). The fragmentation of the intermediate occurring reversibly either toward the initial growing chain (k_{add}) or to free the re-initiating group (R) and a macro chain-transfer agent (macro-CTA) (k_{frag}).

Re-initiation of fragmented radical

The propargyl radical group can then re-initiate polymerization (k_{re-in}) by reacting with the N-vinyl pyrrolidone and start a new polymer chain, which will propagate (k_p) or react back on the macro-CTA (k_{frag}).

Equilibration

This is the fundamental step in the RAFT process which traps the majority of the active propagating species into the dormant thiocarbonyl compound.
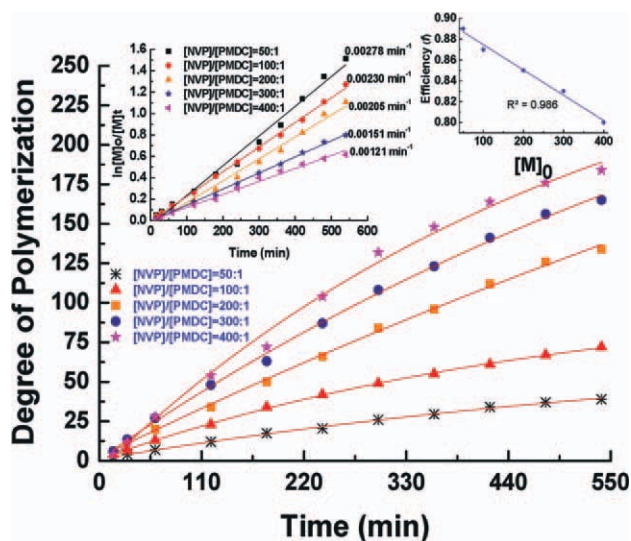

Figure 8 Effect of monomer concentration on RAFT agent efficiency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Experimental Conditions for PMDC_NVP Prepared by RAFT Using PMDC as CTA[a]

Run	Conv.	Time	$\ln[M_0/M_t]$	$M_{n(\text{Theo})}$	$M_{n(\text{GPC})}$	$M_{n(\text{NMR})}$	$M_{n(\text{UV})}$	Đm
1	4	15	0.04082	646	710	670	660	1.50
2	7	30	0.07257	979	1060	920	1020	1.46
3	13	60	0.13926	1646	1810	1430	1730	1.43
4	23	120	0.26136	2757	2970	2310	2900	1.39
5	34	180	0.41552	3980	4370	3310	4680	1.35
6	42	240	0.54473	4869	5180	4090	5730	1.28
7	49	300	0.67334	5647	6210	5200	5880	1.24
8	55	360	0.79851	6314	7020	5980	6720	1.18
9	61	420	0.94161	6981	7840	7090	8120	1.17
10	67	480	1.10866	7647	8600	7540	8310	1.16
11	72	540	1.27297	8203	9430	8310	9220	1.15

[a] $[\text{NVP}] = 1$ Mol.L^{-1}, $[\text{PMDC}] = 1 \times 10^{-2}$ Mol.L^{-1}, $[\text{AIBN}] = 2 \times 10^{-3}$Mol.L^{-1}, temperature = 55°C, time = 9 h, solvent = toluene, initiator efficiency, $f = 0.91$, apparent rate constant (K_{app}) = 2.3 × 10^{-3} min^{-1}and induction time = 2 min (obtained from the slope of ln $[Mo/Mt]$ versus time (t).

This limits the possibility of chain termination. Once the initial CTA has been entirely consumed, the macro-CTA agent is solely present in the reaction medium and enters equilibrium. This equilibrium is considered the main equilibrium, and a rapid exchange between active and dormant (thiocarbonyl-thio capped) chains ensures equal probability for all chains to grow, therefore leading to the production of polymers of narrow molecular weight distribution. Such radical intermediates may also be involved in a variety of side reactions during polymerization, including termination with a propagating polymeric chain.

Termination

It describes the unavoidable reactions of termination present in all free-radical polymerization systems, by either combination (k_{tc}) or disproportionation (k_{td}).

However, as the termination reactions are kept to a minimum, the final product consists of a large majority of polymeric chains showing the re-initiating group (R) at one end and the thiocarbonyl-thio group at the other.

Optimization of reaction parameters

Influence of different mole ratio of different NVP and PMDC

According to the mechanism[4] (Scheme 3), in order to control the polymerization process, increasing the concentration of N-vinyl pyrrolidone after a certain point, was slow down the transformation of PMDC into dormant polymer chains. Therefore, a study of the polymerization of NVP at various molar ratios of $[\text{NVP}]_0/[\text{PMDC}]_0$ was carried out at 55°C. Figure 8 shows the effect of initial monomer concentration with respect to CTA ($[M]_o : [\text{CTA}]_o = 50 : 1$, 100 : 1,

TABLE II
Molar Mass and Conversion Data for Poly(N-Vinyl Pyrrolidone) Samples Prepared Via Different NVP and PMDC Mole Ratio at 55°C

Run	NVP (mmol)	Solvent (mL)	AIBN (mmol)	PMDC (mmol)	$M_{n\text{Theo}}$	$M_{n\text{GPC}}$	Đm	Conv (%)	PMDC/AIBN (mole ratio)
1	100	10	0.2	0.4	6536	6950	1.25	57	2 : 1
2	100	10	0.2	0.6	6981	7590	1.18	61	3 : 1
3	100	10	0.2	0.8	7536	8470	1.16	66	4.1
4	100[a]	10	0.2	1.0	8203	9430	1.15	72	5 : 1
5	100	10	0.2	2.0	10426	13030	1.14	74	10 : 1

Run	NVP (mmol)	Solvent (ml)	AIBN (mmol)	PMDC (mmol)	$M_{n\text{Theo}}$	$M_{n\text{GPC}}$	Đm	Conv (%)	NVP/PMDC (mole ratio)
6	50	10	0.2	1	4535	5100	1.13	78	50 : 1
7	100[a]	10	0.2	1	8203	9430	1.15	72	100 : 1
8	200	10	0.2	1	15094	17760	1.20	67	200.1
9	300	10	0.2	1	18557	22360	1.23	55	300 : 1
10	400	10	0.2	1	20651	25810	1.29	46	400 : 1

[a] $[\text{NVP}] = 1$ Mol.L^{-1}, $[\text{PMDC}] = 1 \times 10^{-2}$ Mol.L^{-1}, $[\text{AIBN}] = 2 \times 10^{-3}$Mol.L^{-1}, temperature = 55°C, time = 9 h, solvent = toluene.
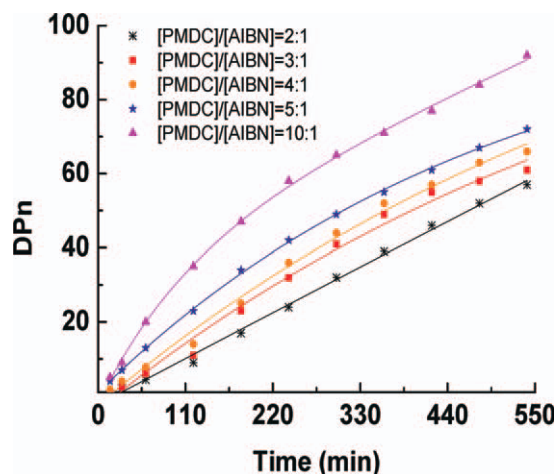
Figure 9 Effect of RAFT agent concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

200 : 1, 300 : 1, and 400 : 1). This plot gave the first-order kinetics for each initial monomer concentration with apparent reaction rate constants, K_{app}, i.e., 2.78, 2.3, 2.05, 1.51, and 1.21 $\times$ 10^{-3}min^{-1}, respectively (Tables I and II). As we increase the [NVP]/[PMDC] ratio, the apparent rate constant decreases from 2.78 $\times$ 10^{-3} min^{-1} to 1.21 $\times$ 10^{-3} min^{-1} and efficiency of CTA decreases from 0.89 to 0.80, respectively, while the degree of polymerization increases continuously. The decrease in percentage of conversion from 78% to 46% is due to the viscosity of the reaction medium, which hinders the movement of the propagating chains towards monomer due to decrement in conversion. However, at 100 equivalents of the [NVP]/[PMDC] ratio, the propagating growth of chain becomes linear (Fig. 5), which supports the controlled polymerization of NVP by PMDC chain transfer agent. Although there was no apparent variation in molar mass dispersity (Đm) with initial monomer percentage conversion, the molar mass dispersity (Đm) increased over the course of the reaction from 1.13 to 1.29 as the mole ratio of [NVP]$_0$/[AIBN]$_0$ increased (Table I, Fig. 8).

Influence of different PMDC and AIBN ratio

Based on the RAFT polymerization mechanism (Scheme 3), the ratio of PMDC and AIBN should have a significant influence on the molar mass dispersity of polymer. Increasing the concentration of initiator or decreasing the concentration of RAFT agent slowed down the transformation of PMDC into dormant polymer chains. At the same time, the probability of termination between two radicals increases. As a result, the obtained polymer has got a broader molar mass dispersity, i.e., 1.14 to 1.25. The influence of different PMDC/AIBN ratio on the molecular weight has been listed in Table II and Figure 9 shows retardation phenomenon in the polymerization process of system. This retardation is due to (i) specificity for the expelled radical to add to the RAFT agent rather than to monomer as the ratio of [PMDC]$_0$/[AIBN]$_0$ increased[43,44] (ii) the cross termination, i.e., the termination between the propagation free radical and intermediate.[45,46]

Effect of temperature

To find out the favorable and optimized temperature for RAFT process, number of experiments was carried out (Table III and Fig. 10) at five different temperatures 45, 50, 55, 60, and 65°C, respectively. As shown in Table III, the conversion and apparent rate constants increases with increase in temperature, among them 55°C was found best reaction temperature for RAFT polymerization of NVP. As shown in runs 1–5 of Table III, % conversion increases from 55 to 80 with increase in temperature from 45°C to 65°C. Thus, when the reaction was performed at 45°C (run 1 of Table III), 55% conversion was observed in 9 h with 1.44 molar mass dispersity. In same time at 50°C (run 2 of Table III), 64% conversion with 1.28 molar mass dispersity, at 55°C (run 3 of Table III), 72% conversion with 1.15 molar mass dispersity, at 60°C (run 4 of Table III), 75% conversion with 1.23 molar mass dispersity and at 65°C (run 5 of Table III), 80% conversion with 1.34 molar

TABLE III
Effect of Temperature Variation to Polymerize N-Vinyl Pyrrolidone with PMDC RAFT Agent

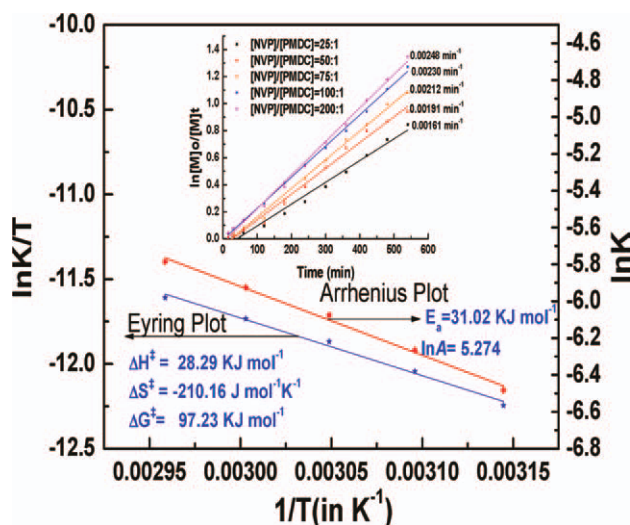| | | | | | Thermodynamic properties | | | | |
| | | | | | Using Arrhenius equation | | Using Eyring equation | | |
T (°C)	% C	$K_{aap \times 10^{-3}}$	$1/T \times 1000$	ln (K/T)	E_a (KJ/mol)	lnA	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
45 (318K)	55	1.53	3.145	−12.2445					
50 (323K)	64	1.90	3.096	−12.0436					
55 (328K)	72	2.30	3.049	−11.8679	31.02	5.27	28.29	−210.16	97.23
60 (333K)	75	2.67	3.003	−11.7338					
65 (338K)	80	3.07	2.959	−11.6091					

Figure 10 Effect of temperature concentration with regard to Eyring and Arrhenius equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mass dispersity were found. Therefore, RAFT polymerization at 55°C is more favorable due to good conversion with narrow molar mass dispersity. The temperature dependency of the apparent rate constants (k_{aap}), the magnitudes of the activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) as well as activation energy (E_a) were determined by evaluation of the resulting straight Eyring correlations through the Eyring and Arrhenius plot for the logarithmic values of the rate constant versus $1/T$ (Fig. 10). The $\Delta S^{\ddagger} \approx -210.16$ J mol^{-1}K^{-1}, the reaction of polymerization shows negative activation entropy which allows a greater flexibility of the activated complex. Due to less rigid structures at the transition state, $^{-}\Delta S^{\ddagger}$ suggests that at transition state, movement of reactants is highly restricted, which supports the progress of the reaction with time. The activation energy E_a (31.02 kJ mol^{-1}) and $\Delta H^{\ddagger}$ (28.29 kJ mol^{-1}) were very close to each other suggesting the feasibility of the reaction.

CONCLUSION

This is the first report of the controlled radical polymerization of NVP with newly synthesized prop-2-ynyl morpholine-4-carbodithioate (PMDC) as chain transfer agent. PMDC reagent was found effective chain transfer agent to polymerize N-vinyl pyrrolidone through RAFT process. The optimized concentration ratio of reactants was found [NVP] : [PMDC] : [AIBN] =100 : 1 : 0.2. Control on the rate of the polymerization was confirmed by the formation of polymer of predetermined molecular weight. The synthesized poly(NVP) shows narrow molar mass dispersity (Đm) between 1.50 and 1.15.

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