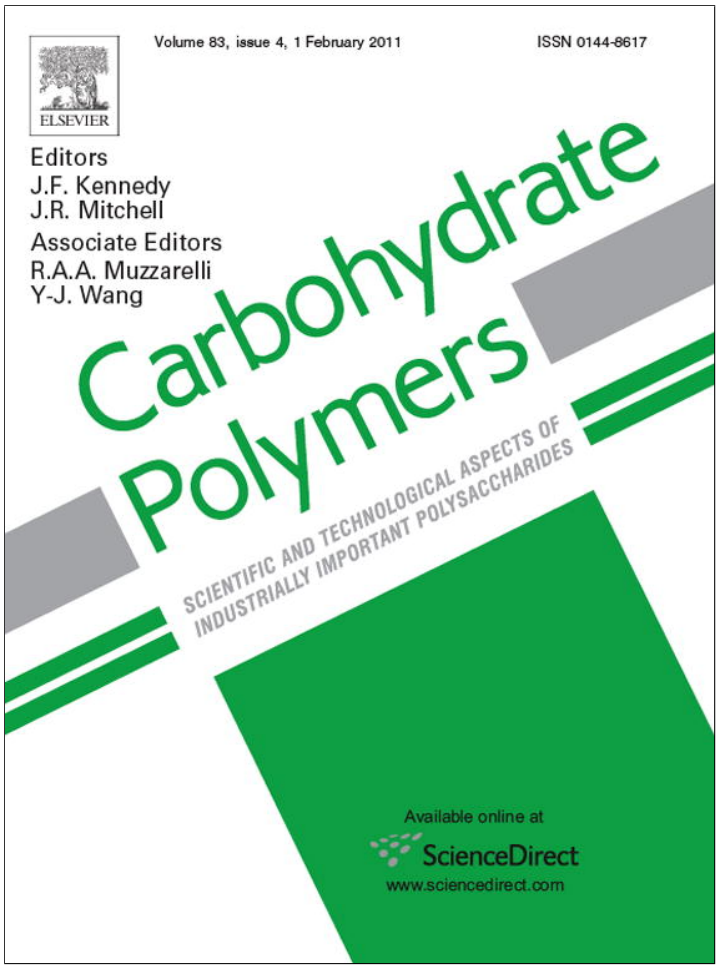

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Synthesis and characterization of five-arms star polymer of N-vinyl pyrrolidone through ATRP based on glucose

Vivek Mishra, Rajesh Kumar*

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

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ABSTRACT

Glucose based five arms atom transfer radical polymerization initiator was synthesized. This initiator was used to synthesize 5-arms star polymer of N-vinyl pyrrolidone (NVP) through controlled radical polymerization. The ratio of reactants were kept as 1:1:2: 200 (initiator:Cu(I)Br:bpy:NVP). The rate of reaction with respect to NVP was found to be first order, and number-average molecular weight increases linearly with temperature up to 90 °C. The activation energy (E_a = 29.75 kJ mol^{-1}) and enthalpy ($\Delta H^{\ddagger}$ = 26.73 kJ mol^{-1}) were found to be in a good agreement with each other for activated complex, and negative value of entropy of activation ($\Delta S^{\ddagger}$ = −219.12 J mol^{-1} K^{-1}) supports the highly ordered transition state.

1. Introduction

In recent years, the main scientific and applied interest in polymeric materials was focused on the development of novel synthetic methods that allow control over the composition of functionality, molecular structure, and molecular weight. During the past decade controlled/living radical polymerization (Kamigaito, Ando, & Sawamoto, 2001; Matyjaszewski & Davis, 2002; Matyjaszewski & Xia, 2001; Yagci & Tasdelen, 2006) became an established synthetic method to prepare new complex architectures of polymer, such as graft (Beers, Gaynor, Matyjaszewski, Sheiko, & Möller, 1998), block (Davis & Matyjaszewski, 2002), star (Matyjaszewski, 2003) and functional polymers with well-defined structures. Nitroxide mediated polymerization (NMP) (Georges, Veregin, Kazmaier, & Hamer, 1993; Hawker, Bosman, & Harth, 2001) or stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) (Kato, Kamigaito, Sawamoto, & Higashimura, 1995; Percec & Barboiu, 1995; Wang and Matyjaszewski, 1995a,b) and reversible addition-fragmentation chain transfer (RAFT) (Barner-Kowollik et al., 2003; Rizzardo, Chiefari, Mayadunne, Moad, & Thang, 2001) processes received considerable interest and have been successfully used for the preparation of macromolecular structures. Amongst them, ATRP appeared to be the most extensively used method because of its easy manipulation, ability to control on molecular weight and structure, and applicability to a wide range of monomers.

Interest in star polymers arises due to their novel properties and topology (for e.g. as viscosity modifiers). They exhibit interesting solution and solid-state properties arising from their three-dimensional shape (Xia, Zhang, & Matyjaszewski, 1999; Zhang, Xia, & Matyjaszewski, 2000). These properties often derive from the their differences in hydrodynamic volume and higher degree of chain end functionality compared to linear polymers of similar composition due to increased intermolecular constraints (Matyjaszewski, Miller, Pyun, Kickelbick, & Diamanti, 1999). A variety of approach has been reported for the synthesis of star polymers (Angot, Murthy, Taton, & Gnanou, 1998; Angot, Murthy, Taton, & Gnanou, 2000). The first approach is which uses living polymerization to prepare the arms followed by quenching with a multi-functional coupling agent, which serves as the core part of polymer (Haddleton & Crossman, 1997; Hadjichristidis, Guyot, & Fetters, 1978; Huber, Burchard, & Fetters, 1984; Morton, Helminiak, Gadkary, & Bueche, 1962). The second approach, often known as the nodule method, which is also based on living polymerization and their propagation followed by cross-linking with divinyl reagents (Kanaoka, Sawamato, & Higashimura, 1991; Worsfold, Zilliox, & Rempp, 1969). This approach is very limited and produces ill-defined star polymers; however, if the coupling termination at this point is minor, it is possible to prepare miktoarm stars using the star polymer as an initiator (Du & Chen, 2004). The final approach is the core first method, which uses a multi-functional initiator to initiate living polymerization and more specifically living radical polymerization (Fujimoto, Tani, Takano, Ogawa, & Nagawawa, 1978; Jacob,

* Corresponding author. Tel.: +91 5426702501.
E-mail address: rkr_bhu@yahoo.com (R. Kumar).

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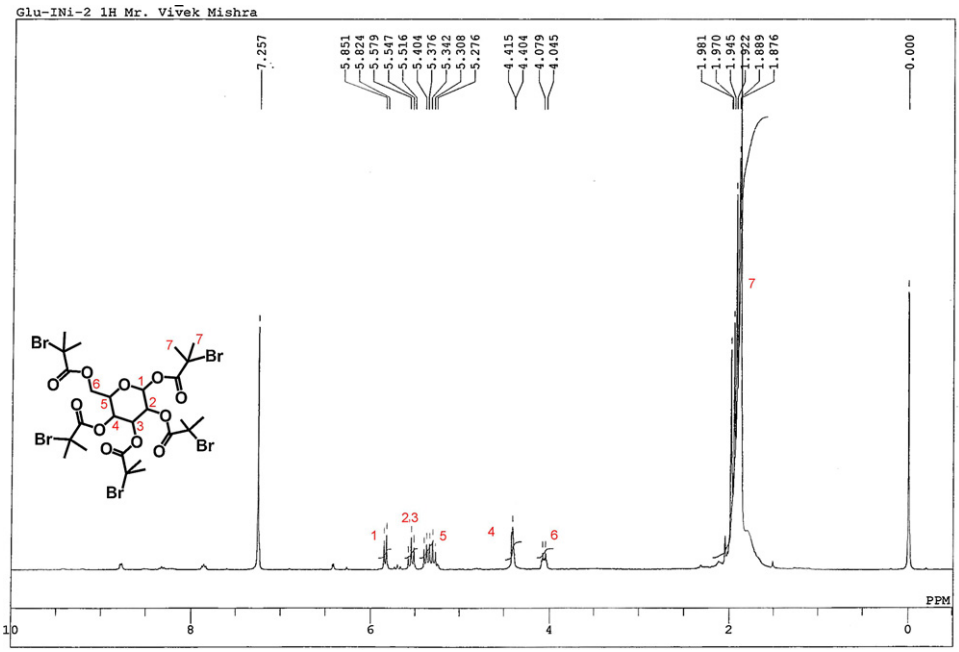


Fig. 1. ^{1}H NMR Spectra of Glucose Initiator in $CDCl_3$.

Majoros, & Kennedy, 1996; Lutz & Rempp, 1988; Shohi, Sawamato, & Higashimura, 1992; Yu, Shi, Guan, An, & Dutta, 2007)

Haddleton, Edmonds, Heming, Kelly, & Kukulj (1999) have reported the preparation of star polymers using cores based on sugars, cyclodextrin (Ohno, Wong, & Haddleton, 2001), aromatic alcohols (Narrainen, Pascual, & Haddleton, 2002). Angot, Taton, & Gnanou (2000) and Matyjaszewski, Qin, Boyce, Shirvanyants, & Sheiko (2003) have used also branched alcohols to achieve similar effects. Ejaz, Ohno, Tsujii, & Fukuda (2000) have adopted ATRP to graft glycopolymers and to attach to a solid surface. Thus, one approach for glycopolymer synthesis is to utilize living radical polymerization (Darling et al., 2000) in combination with monomers or initiators that contain sugar residues. The functionality of sugars can also be utilized as an efficacious route to star polymers (Limer et al., 2006; Stenzel-Rosenbaum, Davis, & Fane, 2001). Molecules such as glucose and sucrose have significant advantages as part of a general synthetic strategy, as they are cheap, are readily available, and can easily be hydrolyzed under mild conditions to retrieve and assess the polyarms.

Similarly, poly N-vinyl pyrrolidone (PNVP) is a synthetic, nontoxic, water-soluble polymer commonly used in wide range of applications including several pharmaceutical purposes/uses/formulations. A disadvantage of PNVP is the lack of a reactive group, which limits its chemical modification. PNVP polymers are film formers, protective colloid and suspending agents, dye-receptive agents, binders, stabilizers, detoxicants, and complexing agents (Barabas et al., 1990). Moreover PNVP form complex with iodine (PNVP-I) which is a bactericide with various attractive merits, such as broad spectrum, high efficiency, non-irritation, and persistence (Xing, Deng, & Yang, 2005). Importance of PNVP has been increasing due to its potential biological activity. Glycopolymers (Okada, 2001) are of interest as molecular recognition which plays important roles in many biological processes including viral/bacterial infection (Spaltenstein & Whitesides, 1991) and fertilization (Wasserman, 1987) etc.

We are exploiting ATRP using copper (I)/bpy complex for the controlled radical polymerization of NVP and extending this to the synthesis of polymers with a range of novel functionality and topology. This work reports some initial results, which demonstrate some of the principles of this strategy. We selected the extremely versatile ATRP technique to prepare glucose-based five-arms star polymers of N-vinyl pyrrolidone.

2. Experimental

2.1. Materials

N-vinyl pyrrolidone (NVP) (Aldrich, 99%) was distilled at 60 °C and 8 mm Hg prior to the experiments in order to get pure NVP. 2,2′-Bipyridine (bpy) and 2-bromo isobutyrylbromide were from Aldrich with purity (98–99%). D(+)-Glucose (Sigma, 99.5%) was purchased and used as received. Copper (I) bromide (Aldrich, 99%) was washed with glacial acetic acid in order to remove any oxidized species, filtered, washed with ethanol, and dried. Toluene (Merck, 99.9%) was refluxed under nitrogen with calcium hydride, distilled and stored over activated molecular sieves under nitrogen atmosphere. Other liquid reagents and solvents were deoxygenated by purging nitrogen gas for several hours prior to use. Dichloromethane and triethylamine were dried on calcium hydride and distilled prior to use.

2.2. Chemical analyses

^{1}H NMR analysis: ^{1}H NMR spectra were recorded on a JEOL AL300 FTNMR (300 MHz) at ambient temperature in DMSO-d_6 and $CDCl_3$ as solvent and are reported in parts per million (ppm) from internal tetramethylsilane or residual solvent peak.

FTIR analysis: FTIR spectra of the samples was recorded by making pellets in KBr using a Varian Excalibur 3000 (Palo Alto, CA). The FTIR spectral analyses were used to prove the synthesis of initiator and polymerization reaction.

UV–vis analysis: The UV–vis spectra of Penta-*O*-isobutyryl bromide-α-D-glucose (PIBBG) and poly (N-vinyl pyrrolidone) based on glucose (PIBBG_NVP_Br) were recorded in toluene on PerkinElmer–Lambda 35 UV–vis Spectrophotometer at room temperature 25 °C. The optical path length of measurement cell was 10 mm.

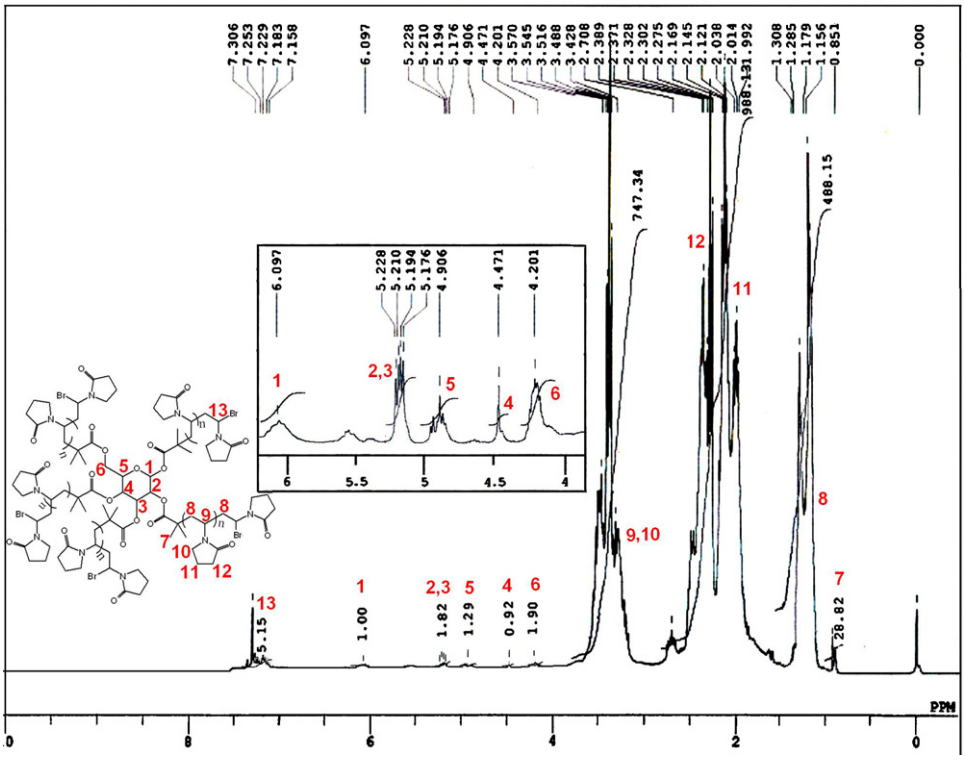


Fig. 2. ^{1}H NMR of PIBBG_NVP_Br polymer in $CDCl_3$.

GPC analysis: Number average molecular weights (M_n), weight average molecular weights (M_w) and molar mass distribution ($Đ_m$) of polymers were measured at 40 °C on a Polymer Laboratories PL GPC-220 using THF as a solvent. Calibration was done by Polymer Laboratories detector software Cirrus with PMMA-standard.

2.3. Different formulae for calculation of parameters

$$\%\ \text{Gravimetric Conversion} = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (1)$$

$$\text{Conversion by } {}^1\text{HNMR} = \frac{A_{\text{Polymer integral peak}} - A_{\text{vinyl monomer integeral peak}}}{A_{\text{Polymer integral peak}}} \quad (2)$$

All monomers conversions for the kinetic study were determined by ^{1}H NMR with the samples directly withdrawn at specific time intervals. It was estimated by comparing the peak areas of the monomer and homopolymer.

$$M_{n\ \text{NMR}} = M_{\text{PIBBG}} + M_{\text{NVP}} \times \frac{[M_{\text{NVP}}]_0}{[M_{\text{PIBBG}}]_0} \times \text{Conversion} \quad (3)$$

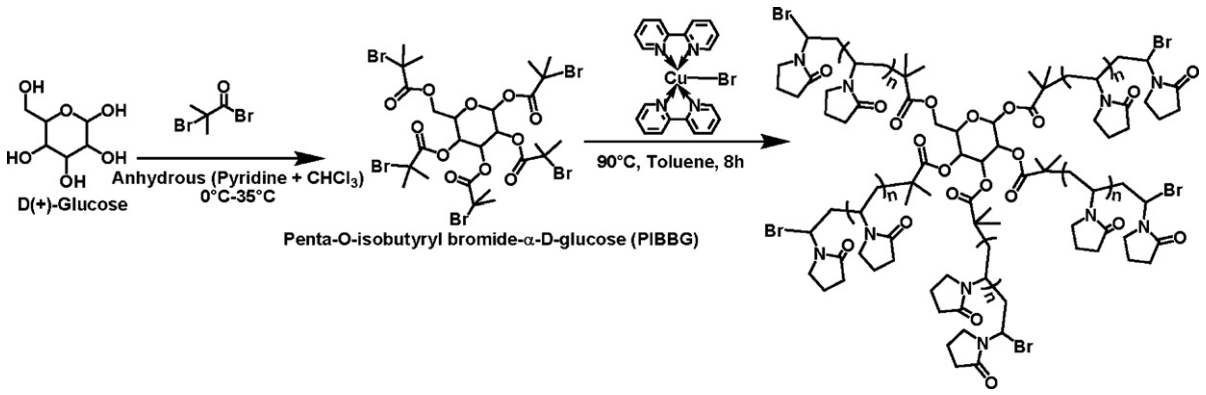
$$M_{\text{n (Theoratical)}} = \frac{[\text{NVP}]_o}{[\text{PIBBG}]_o} \cdot X_{\text{NVP}} \cdot M_{\text{NVP}} + M_{\text{PIBBG}} \quad (4)$$

$$M_{\text{n (UV)}} = \frac{w}{c_{\text{PIBBG}}} \quad \text{[Qiu, Tanaka, Winnik, 2007]} \quad (5)$$

$$\text{Initiator efficiency, } f = \frac{M_{\text{n theo}}}{M_{\text{n SEC}}} \quad (6)$$

$$\text{Total concentration of propagating chains, } [P*] = f\,[I]_0 \quad (7)$$

$$\text{Degree of polymerization (DP)} = \frac{[\text{NVP}]_0}{[\text{PIBBG}]_0} \times \text{Conversion} \quad (8)$$



Scheme 1. Reaction conditions of synthesis of PIBBG initiator and their ATRP polymer.

2.4. Precursor (glucose) possesses following structural characteristics

^{1}H NMR (300 MHz, DMSO-d_6,): δ 6.202–6.187 (1H, d, J = 4.5 Hz, anomeric), 4.896 (1H, C_3), 4.764–4.746 (1H, d, J = 5.4 Hz, C_4), 4.627–4.611 (1H, d, J = 4.8 Hz, C_5), 4.450–4.334(2H, m, J = 6.6, 5.4 Hz, C_6), 3.571–3.404 (4OH,br d, s, q, J = 3.9, 5.1 Hz, $C_{1,2,3,4}$), 3.099–3.038 (1H, t, J = 9.3 Hz), 3.019 (1OH, br s, C_6) [Fig. S1].

FTIR (KBr, cm^{-1}): 3600–3000($\nu_{OH1-6,\,str}$), 2970($\nu_{CH2\ band\ of\ CH2-O-,\,str}$), 2935($\nu_{CH\ and\ CH3,\,str}$), 2913($\nu_{CH\ str\ of\ C3,\,4,\,and\ 5}$), 2865 ($\nu_{CH\ str\ of\ C6}$), 2850($\nu_{CH\ str\ of\ C2}$), 1494($\nu_{deformation\ vibration\ of\ methylene\ group}$), 1455, 1443, 1420, 1390($\nu_{aggregate\ of\ deformational\ CCH\ and\ OCH\ vibrational\ stretching}$), 1356($\nu_{CCH\ of\ C4,\,str}$), 1327, 1320, 1308, 1298, 1280($\nu_{overlapping\ band\ due\ to\ intense\ vibration\ of\ C4}$), 1147 and 1120 ($\nu_{characteristics\ of\ cyclic\ structures\ of\ monosaccharide\ in\ which\ 1147\ and\ 1120\ for\ \alpha\text{-D-glucose}}$), 917–840($\nu_{two\ broad\ mutually\ distant\ intense\ narrow\ bands\ of\ \alpha\text{-D-glucose}}$), 820–600($\nu_{torsional\ vibrations\ of\ the\ C-O\ bond\ of\ the\ hydroxyl\ groups\ appears}$) [Fig. S2]. UV (DMSO): 230 nm [Fig. S3].

2.5. N-vinyl pyrrolidone as monomer

^{1}H NMR spectrum in $CDCl_3$ 300 MHz (δ, ppm): δ 7.18–7.02 (1H), 4.31–4.42 (2H), 3.58–3.42 (2H), 2.56–2.42 (2H) and 2.18–2.02 (2H). IR spectrum (KBr plates, cm^{-1}): 3482, 2973, 2890, 1699, 1630, 1427, 1390, 1330, 1282, 1043, 982, 850, 640 [Fig. S2].

2.6. Initiator synthesis: penta-O-isobutyryl bromide-α-D-glucose (PIBBG)

Glucose (50 g, 0.278 mol) was suspended in a mixture of anhydrous pyridine (200 mL) and anhydrous chloroform (350 mL) under an atmosphere of nitrogen at 25 °C. The suspension was cooled to 0°C and a solution of 2-bromoisobutyryl bromide (205 mL, 1.67 mol) in anhydrous chloroform (100 mL) was added dropwise over a period of 1 h. The reaction mixture was heated at 35 °C with stirring for 4 days. Later, the reaction mixture was diluted with chloroform (300 mL), washed successively with ice-water (500 mL), saturated aqueous sodium hydrogen carbonate solution (500 mL × 3) and finally with water (500 mL). Dried on $MgSO_4$, filtered and evaporated to give a pale orange cake. Further, methanol (1L) was added and the suspension was stirred vigorously to break up the cake into fine suspension. The solid was filtered, washed with methanol (2 ×500 mL) and dried to give the desired product (214.3 g, 84%) as a white powder. M_p = 211 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) 5.851–5.824 (d, 1H, anomeric), 5.579–5.516 (m, 2H, CH), 5.404–5.276 (d & t, 1H, CH), 4.415–4.404 (d, 1H, CH, CH) 4.404–4.045 (d, 2CH), 1.981–1.876 (m, br, 30H, 2) [Fig. 1]. FTIR: 3467, 2979, 2930, 1747($\nu_{C=O}$), 1462, 1386, 1267, 1154 and 1105($\nu_{characteristics\ of\ cyclic\ structures\ of\ monosaccharide\ in\ which\ for\ \alpha\text{-D-glucose}}$), 1009, 966 and 858 ($\nu_{two\ broad\ mutually\ distant\ intense\ narrow\ bands\ of\ \alpha\text{-D-glucose}}$), 834($\nu_{torsional\ vibrations\ of\ the\ C-O\ bond\ of\ the\ hydroxyl\ groups\ appears}$) 654($\nu_{C-Br,\,str}$) [Fig. S2], UV (DMSO): λ_{max} = 257 nm [Fig. S3]. The obtained spectral analyses were matched with the reported literature elsewhere [Limer et al., 2006].

2.7. Polymerization procedure

0.173 g of 1,2,3,4,6-penta-*O*-isobutyryl bromide-D-glucose (1), 0.347 g of bpy, 10 mL of toluene and 10 mL of NVP were added to a three neck round bottom flask and then the whole solution was purged with N_2. Three-freeze pump thaw cycle was performed to remove dissolved oxygen. Then 0.135 g of CuBr was added to the frozen solution, and again freeze pump thaw cycle was performed again and finally flask was purged with nitrogen gas. The flask was then placed in an oil bath at 90 °C. The polymerization was monitored at regular time intervals by ^{1}H NMR and % conversion is calculated. After a desired time, the reaction mixture was removed, diluted with toluene (100 mL), filtered through a column of basic alumina to remove the copper catalyst and the filtrate was evaporated under reduced pressure. Again polymer was dissolved in chloroform (120 mL) and added dropwise to petroleum ether (BP = 40–60 °C) with vigorous stirring to precipitate the polymer. The solvent was removed by rotary evaporator to get final product, the star polymer.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.306–7.158 (dd, 5H, C_{13}), 6.097 (s, 1H, C_1), 5.228–5.176 (dd, 2H, $C_{2,3}$), 4.906 (br, s, 1H, C_5), 4.471 (br, s, 1H, C_4), 4.201 (br, s, 2H, C_6), 3.570–3.428 (br, m, $C_{9,10}$), 2.389–2.169 (br, m, C_{12}), 2.145–2.192 (br, m, C_{11}), 1.308–1.156 (dd, 1H,C_8), 0.851(br, s, C_7) [Fig. 2]. IR spectrum (KBr plates, cm^{-1}): 3600–3400 ($\nu_{due\ to\ absorbed\ moisture}$), 2979 ($\nu_{CH\ str}$), 2930($\nu_{CH\ and\ CH3,\,str}$), 1696($\nu_{N-CO-,\,str.\ for\ cyclic\ tertiary\ amide}$), 1426($\nu_{C-N\ str.}$), 1149 and 1122($\nu_{characteristics\ of\ cyclic\ structures\ of\ monosaccharide\ for\ \alpha\text{-D-glucose}}$), 696 ($\nu_{C-Br,\,str}$) [Fig. S2]. UV spectra (DMSO): 230 nm (glucose moiety), 257 (PIBBG initiator) and 379 nm (PIBBG_NVP polymer) [Fig. S3].

3. Results and discussion

The penta functional atom transfer radical polymerization (i.e. penta-*O*-isobutyryl bromide-α-D-glucose) initiator (**1**), was prepared via the reaction of α-D-glucose with 2-bromoisobutyrlbromide (Scheme 1). Under these conditions, the stereochemistry of the anomeric carbon remains intact with a small amount of the β-D-glucose arising from contamination of the starting material.

The bromide terminated well-controlled poly (N-vinyl pyrrolidone) (PIBBG_NVP) was synthesized by using ATRP process. The feed molar ratio of $[NVP]_0$: $[PIBBG]_0$:$[CuBr]_0$:$[bpy]_0$ (200:1:1:2) was maintained in the mixture by adding N-vinyl pyrrolidone 23 mL (18.94 g, 240 mmol), initiator 0.11 g (1.2 mmol), ligand 0.37 g (2.4 mmol) and catalyst 0.172 g (1.2 mmol). This mixture was placed in a three-neck reactor containing 23 mL degassed toluene and teflon coated magnetic bar. The solution was purged with purified and dried nitrogen gas for 30 min. The deoxygenated solution was equally divided into ten dried and deoxygenated polymerization glass tubes. Then, the polymerization tubes were placed in a thermostatic bath at 90 °C for the desired time. The reaction was stopped by freezing the reaction mixture by using liquid nitrogen. The PIBBG_NVP terminated by Br was diluted with toluene (100 mL) and filtered through a column of basic alumina to remove the Cu(II)/bpy complex. The filtrate was evaporated under reduced pressure and the polymerization was confirmed by ^{1}H NMR analyses (Fig. 2). The –CH replaced by Br of repeating unit of NVP (indicated as C_{13}) appears as a double doublet at 7.306–7.158, 6.097 ppm singlet for anomeric glucose proton (indicated as C_1), double doublet for proton of C_2 and C_3 of glucose 5.228–5.176 ppm, broad singlet appears for protons of C_4, C_5 and C_6 (as indicated in Fig. 2) at 4.471, 4.906 and 4.201 ppm respectively. The –CH and N–CH_2 (indicated as C_9, C_{10}) repeating units of NVP appear at 3.570–3.428 ppm as a broad multiplet. Proton of C_{11} and C_{12} (as indicated in Fig. 2) of NVP appear as a broad multiplet at 2.145–2.192 and 2.389–2.169 ppm respectively. The CH_2 repeating unit of NVP (indicated as C_8, Fig. 2) appears as a double doublet at 1.308–1.156 ppm, and the methyl group of initiator moiety appears at 0.851 ppm as a singlet (Fig. 2). The disappearance of broad band of–OH (3600–3000 cm^{-1}) of glucose by the appearance of cyclic tertiary amide at 1696 cm^{-1} for N–C=O and 1426 cm^{-1} for C-N stretching of NVP. The band of initiator at 2930 cm^{-1} for –CH and –CH_3 stretching, 1149 and 1122 cm^{-1} for cyclic structure of monosaccharide of α-D glucose and 696 cm^{-1} for C–Br stretching, these bands of FTIR spectra of polymer supports the successful ATRP polymerization of NVP (Fig. S2). UV analyses shows the peak

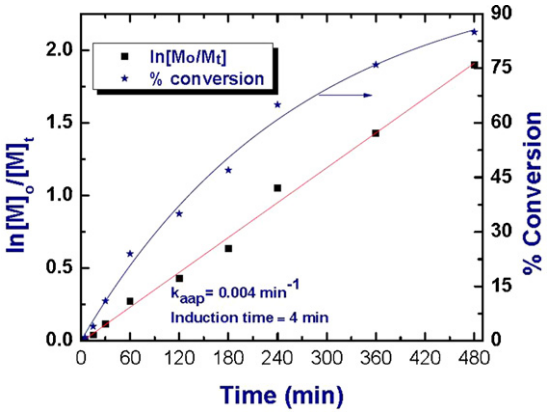


Fig. 3. Plot of time versus monomer conversion and $\ln[M]_o/[M]_t$.

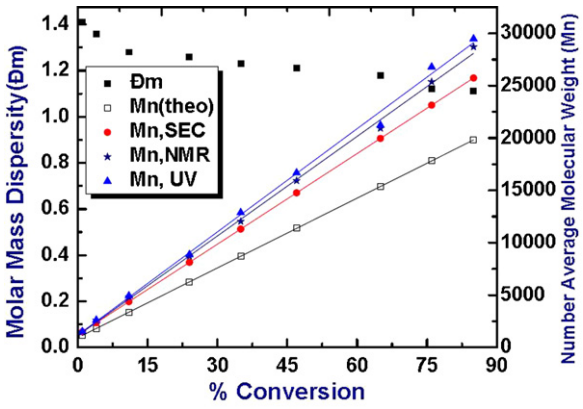


Fig. 4. Plot of NVP polymerization among M_n through theoretically, SEC, NMR and UV and Molar mass distribution of PIBBG_NVP_Br as a function of NVP monomer conversion in toluene at 90 °C in the presence of $[Cu(I)Br]_o$:$[PIBBG]_o$:$[bpy]_o$ = 1:1:2.

of glucose and initiator at 230 and 257 nm which is due to n–π* transition of –OH of glucose and π–π* transition of –C=O of isobutyryl moiety of initiator respectively (Fig. S3). The presence of these peaks and one additional peak at 379 nm in polymer which is due to the π–π* transition of tertiary amide of NVP further supports the successful polymerization.

The conversion by GPC chromatogram (Fig. S4) obtained for PIBBG_NVP is unimodal and narrow molar mass distribution (1.11) at 85% conversion. The conversion of monomer to polymer was good to retain a degree of chain end functionality. Monomer conversions were also determined by ^{1}H NMR (Fig. 1) by comparing the integrated peak area of residual vinylic signals at δ 4.31–4.42 (2H) ppm and δ 6.99 (1H) ppm of the monomer with that of the peak at δ 1.156–1.308 (2H, C_8) ppm and 3.428–3.570 (1H, C_9) ppm of the corresponding polymer. Finally, the polymer was dissolved in chloroform (120 mL) and added dropwise to petroleum ether with vigorous stirring to precipitate the polymer. The solvent was removed by suction to give 5 arms (PIBBG_NVP_Br) star polymer and dried under vacuum oven at 35 °C for 10 h.

4. Optimization of reaction parameters

4.1. Effect of initiator concentration

The PIBBG initiator is expected to control the polymerization process and the growth of chains in a constant way. A fast initiation step is required to ensure the polymer growth. Due to the tertiary carbon centre, the C–Br bond is enough to promote the initiation. Thus, this initiator has good efficiency to generate polymer chain. For its concentration effect on polymer growing chains, 1, 2 and 6 equivalent of PIBBG was used with respect to catalyst (Table S1). The monomer conversion decreased and the molecular weight distribution increased with increasing concentration of PIBBG-initiator. This suggests that the high initiator concentration shifts the ATRP equilibrium towards Cu(II) species and radicals resulting in the uncontrolled polymerization [Fig. S5]. Thus the best ratio is found to be 200:1:2:1 ([NVP]:[PIBBG]:[bpy]:[Cu(I)]).

4.2. Effect of initial monomer concentration

Fig. 5 shows the effect of initial monomer concentration with respect to initiator ($[M]_o$:$[I]_o$ = 100:1, 200:1 and 400:1). This plot gave the first-order kinetics for each initial monomer concentration with apparent reaction rate coefficient, K_{app} of 2.4, 4.0 and 5.3×10^{-3} min^{-1} respectively (Tables 1 and S2). Reaction with 100 equivalents of NVP gave 93% conversion with 1.21 molar mass distributions whereas 400 equivalents NVP gave 67% conversion with 1.38 molar mass distributions. The decrease in percentage of conversion is due to the viscosity of the reaction medium. However, the reaction with 200 equivalents of NVP, the propagating growth of chain became linear [Fig. 3], which supports the controlled polymerization of NVP by PIBBG initiator.

Within the above reaction conditions, DP_n increases linearly with percentage conversion and it is large at high initial monomer concentration ranging from DP_n = 93 at $[M]_o$:$[I]_o$ = 100:1 to DP_n = 268 at $[M]_o$:$[I]_o$ = 400:1 [Fig. 5]. Although there was no apparent variation of $Đ_m$ with initial monomer percentage conversion, the $Đ_m$ decreased over the course of the reaction from 1.41 to 1.11. [Table 1, Fig. 4]. Although it is expected that an increase in initial monomer concentration would affect the activity of the catalyst due to ligand-monomer binding, but the effect was negligible due to solvation of the monomer in the medium.

4.3. Effect of solvent on polymerization

Due to the excellent solubility of complex Cu(I)Br/bpy in toluene or even in pure monomer, the influence of the polarity of the

Table 1
Experimental conditions for PIBBG_NVP_Br prepared by normal ATRP using PIBBG as initiator[a]

%Conv.	Time (min)	$\ln[M_0/M_t]$	$M_{n\,(theo)}$	$M_{n\,(SEC)}$	$M_{n\,(NMR)}$	$M_{n\,(UV)}$	$Đ_m$
1	5	0.01005	1147	1712	2036	1894	1.41
4	15	0.04082	1814	2708	3148	2608	1.36
11	30	0.11653	3370	5030	5371	4934	1.28
24	60	0.27444	6260	9343	9261	8875	1.26
35	120	0.43078	8705	12,992	12,039	11,879	1.23
47	180	0.63488	11,372	16,973	15,929	15,674	1.21
65	240	1.04982	15,373	22,945	20,930	19,024	1.18
76	360	1.42712	17,818	26,594	25,376	26,783	1.12
85	480	1.89712	19,819	29,580	28,710	27,472	1.11

[a] [NVP] = 2 mol L^{-1}, [Cu (I) Br] = 1×10^{-2} mol L^{-1}, [PIBBG] = 1×10^{-2} mol L^{-1}, [bpy] = 2×10^{-2} mol L^{-1}, temperature = 90 °C, time = 8 h, solvent = toluene, initiator efficiency, f = 0.67, [P^*] = 1.28×10^{-2} mol L^{-1}, apparent rate constant (K_{app}) = 4.0×10^{-3} min^{-1} (obtained from the slope of ln [M_o/M_t] versus time (t) (fig.), $t_{1/2}$ = 144.1 min.

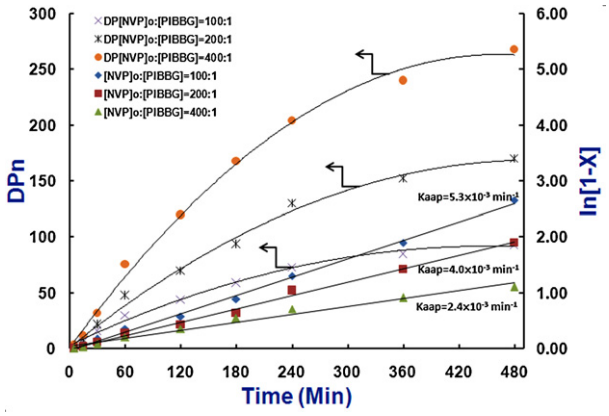


Fig. 5. Effect of monomer concentration on conversion and DP_n.

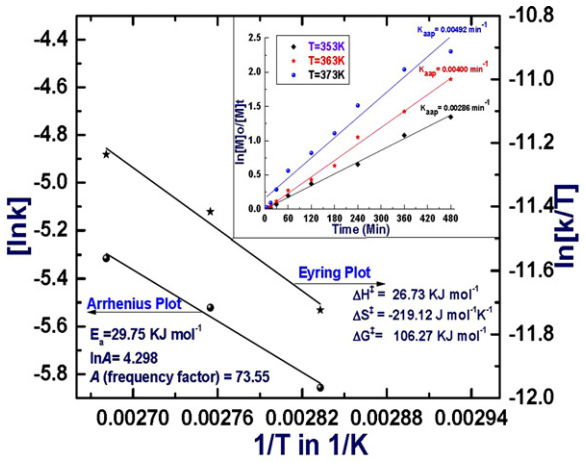


Fig. 6. Eyring and Arrhenius plot w.r.t. rate constants *vs.* 1/*T*. [in inset] Effect of Temperature on initial concentration of monomer at time.

media in the ATRP of NVP has been investigated by varying the toluene/monomer ratio. As shown in Table S3 (entry 1) when reaction was carried out in pure monomer, a 92% conversion of the monomer was observed within 5 h. The rate decreases when excess toluene is used which is due to the decrease in polarity and/or of monomer concentration. On the other hand, it seems that the variation of polarity of the reaction medium does not play a perceptible effect in the control of molar mass distributions in the Cu(I)Br/bpy catalyzed reaction. The absence of influence of the solvent polarity is in good agreement with an inner-sphere electron transfer for both activation and deactivation redox steps (Nanda and Matyjaszewski, 2003a,b).

4.4. Effect of Cu (I)/bpy ratio concentration

To check the effect of ligand concentration 1, 2 and 3 equivalent of bpy with respect to Cu(I)Br catalyst has been taken. It was observed that the 1 equivalent bpy gave 53% conversion (after 12 h) but oligomers with 1.26 molar mass distribution, because in the less polar media, Br^- is destabilized and concurrently binds much stronger to Cu(I)Br than bpy does, resulting in $Cu(bpy)_2{}^+CuBr_2{}^-$ species (Fig. S6). 2 equivalent of bpy gave 85% conversion with 1.11 molar mass distribution and 3 equivalent bpy gave 87% conversion with 1.33 molar mass distribution [Table S4]. It is due to the excess of bpy (more than 2:1) which cannot displace Br^- from the dibromocuprate anion ($CuBr_2{}^-$). The $CuBr_2{}^-$ is inactive and does not participate in the ATRP activation process (Matyjaszewski, Patten, & Xia, 1997; Levy, Olmstead, & Patten, 2000). Therefore, only half of the copper species is involved in the activation of Cu (I) cation, thus net change in the conversion is almost constant.

4.5. Effect of temperature

To found the ambient temperature for ATRP process, three experiments were carried out at different temperatures 80, 90 and 100 °C. As shown in Table S5, the conversion increases with increase in temperature. Thus, when the reaction was performed at 100 °C, 90% conversion was observed in 8 h with 1.09 molar mass distributions. At 90 °C, 85% conversion in 8 h with 1.10 molar mass distribution and at 80 °C, we found only 84% conversion in 12 h with 1.43 molar mass distribution. Therefore, polymerization at 90 °C is more favorable due to higher yield and narrow molar mass distribution with a good control on polymerization [inset of Fig. 6].

The temperature dependency of the apparent rate constants (k_{aap}) was studied and the magnitudes of the activation enthalpy ($\Delta H^‡$) and activation entropy ($\Delta S^‡$) as well as activation energy (E_a) were determined by Eyring correlations [Fig. 6]. The error levels were calculated from the standard deviation of the Eyring and Arrhenius plots for the logarithmic values of the rate constants versus 1/*T*. The $\Delta S^‡ \approx -219.12\,J\,mol^{-1}\,K^{-1}$, the reaction of polymerization shows negative activation entropy, which is due to the sterically less demanding bromide moiety. This allows a greater flexibility of the activated complex due to less rigid structures at the transition state and the value of $-\Delta S^‡$ suggests that the transition state is highly ordered than the reactants. The activation energy (E_a) ($29.75\,kJ\,mol^{-1}$) and $\Delta H^‡$ ($26.73\,kJ\,mol^{-1}$) were very close to each other and supporting the feasibility of the reaction.

5. Conclusion

The polymerization of NVP by ATRP process was successfully carried out to get glucose based 5-arms star polymer. The synthesized polymer shows narrow molar mass distribution between 1.41 and 1.11. Molecular weights obtained by different methods are quite close to theoretical value. The activation energy ($E_a = 29.75\,kJ\,mol^{-1}$) and activation enthalpy ($\Delta H^‡ = 26.73\,kJ\,mol^{-1}$) were very close to each other, supporting the progress of the reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2010.10.004.

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