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Synthesis of internal- and mid-alkyne functional polystyrene by atom transfer radical polymerization

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Abstract
Well-defined alkyne functional polystyrenes were prepared using α-bromoesters 2-bromo-2-methyl-propionic acid-4-hydroxy-but-2-ynyl ester (BPE) and 2-bromo-2-methylpropionic acid-but-2-ynyl diester (BPDE) as initiator by Cu-mediated Atom Transfer Radical Polymerization (ATPP) of styrene. The polymerization of styrene with BPE gives polystyrene containing internal-alkyne functionality whereas BPDE system gives polystyrene containing mid-alkyne functionality. In case of both α-bromoester initiators, the molecular weight of the polymer obtained was increased linearly against conversion keeping narrow molecular weight distribution. The molecular weight and molecular weight distribution of all the polymers were determined by Gel Permeable Chromatography (GPC) analysis. The structures of internal-alkyne and mid-alkyne functional polystyrenes were confirmed by ^{1}H NMR spectroscopy.

Keywords: Functional polymer, alkyne-functional polymers, atom transfer radical polymerization (ATRP), Well-defined polymers

1. Introduction
Functional polymers are valuable materials because of the possibility of tailoring the chain structure as well as their applications. [1] Alkyne functional polymers are reactive macromolecules which have capability of coupling to other polymers or small molecules containing azide group through azide-alkyne [2-4] click reaction and they have various applications in surface modification [5], adhesion [6], drug delivery [7], compatibilization of polymer blends [8-9], designing of complex molecular architectures; e.g, synthesis of macromonomers [10], branched polymers [11], cross linked polymers [12], graft polymers [13] and cyclic polymers [14] etc. To date, numerous click chemistry-based strategies (terminal alkyne-azide cycloaddition) have been reported for the modification of surfaces i.e., micro- and nanoparticles using end-alkyne functional polymers. Ranjan and Brittain [15] combined living radical polymerization with click chemistry to modify the surface of silica nanoparticles with polymers. The possibilities of post-functionalization of poly(6-azidohexyl methacrylate)-grafted silica nanoparticles with various functional alkynes via click reactions were also demonstrated by Li and Benicewicz. [16] Using Cu-catalyzed click reaction, the modification of polymeric particles with azide- or alkyne-functionalized dyes and macromolecules was successfully achieved in aqueous and nonaqueous environments. [17-19] The versatility of copper-catalyzed alkyne−azide coupling (CuAAC) in functionalizing drug-loaded polymeric nanoparticles was demonstrated via the modification of surface of acetylene-functionalized nanoprticles with folate, biotin, and gold nanoparticles. [20] A novel well-defined cyclic poly(ethylene oxide)-b-polystyrene was synthesized via click chemistry using polyethylene oxide-alkyne and polystyrene-azide as precursor. [21]

Atom transfer radical polymerization (ATRP), a controlled radical polymerization allows for the polymerization of a wide range of monomers such as styrenes [22-24], acrylates [25] and methacrylates [26-27] and produced well-defined polymer chain. ATRP tolerates many functional groups; thereby facilitating the preparation of highly functionalized polymers. [28] Matyjaszewski *et al.* [29] synthesized an alkyne terminated ATRP initiator to synthesis well-defined α-alkyne-ω-bromo-terminated polystyrene. They [30] also prepared alkyne end-functional linear poly(styrene) precursors using propargyl-2-bromoisobutyrate as initiator with ATRP technique. But a variety of side reactions were observed by using terminal alkyne functional initiator in ATRP, such as, oxidative alkyne−alkyne coupling, [31-33, 33] formation of cuprous acetylides, [34] radical addition across the triple bond, [35] and chain transfer of the radical with propargylic atoms [36].

Occasionally the acetylenic position of terminal alkyne functionalized ATRP initiators are protected using a silicon-protecting group in order to prevent "copper complexation" [37] or cuprous acetylide formation and other unspecified "side reactions". [38, 39-42]

Although several examples are reported for synthesis of terminal alkyne-functional polymers and tailoring the polymer chain by alkyne-azide click reaction, the synthesis of mid alkyne-functional polymers and their uses as precursor in click reactions are rare. Recently, J. Guochen *et al.* reported Ru-mediated click reaction between organic azides and terminal or internal alkynes for small molecules. [43] Very recently, copper-free azide and mid-alkyne click chemistry was utilized to covalently modify polyvinyl chloride by B. Rebecca. [44] The macromolecules with internal or mid-alkyne groups, therefore have grate potential for further modification by azide-alkyne click reaction. The well-defined clickable macromolecule precursors with internal or mid-alkyne group could be synthesized by tuning the functionality of the initiator in ATRP system. Therefore, in the present work, internal alkyne- and mid alkyne-functionalized polystyrenes were synthesized by Cu (I)-bypiridine mediated ATRP of styrene using 2-bromo-2-methyl-propionic acid-4-hydroxy-but-2-ynyl ester (BPE) and 2-bromo-2-methylpropionic acid-but-2-ynyl diester (BPDE) as initiator**.**

2. Experimental

2.1 Materials: Styrene and 2, 2′-bipyridine was purchased from Sigma Aldrich and were used as received. CuBr was purchased from Sigma Aldrich and was purified by washing with diethylether and further drying in an oven overnight at 60 °C. BPE and BPDE were synthesized which was previously reported. [45] All the solvents used in this work were purchased from Fluka.

2.2 Analytical Procedures: ^{1}H NMR analysis of polystyrene was carried out with BRUKER Spectrometer operated at 400 MHz in pulse Flourier Transform mode using chloroform-*d* as solvent. The peak of chloroform-*d* (7.26 ppm) was used as internal reference. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polystyrene was measured by GPC (Waters 150 C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^{1}H NMR spectrum of polymer was recorded at room temperature on a BRUKER spectrometer operated at 400 MHz in pulse Fourier Transform mode with chloroform-*d* as solvent. The peak of chloroform-*d* (7.23 ppm) was used as internal reference.

2.3 Synthesis of Internal- and Mid-Alkyne functional Bromoesters: The two new initiators BPE and BPDE were synthesized according to a method described by Kabir Homayun *et al.* [45]

^{1}H NMR of BPE initiator: ^{1}H NMR ($CDCl_3$): 1.85 ppm (S, 6H, -C(Br)$(CH_3)_2$, at 3.84 ppm (broad, 1H, -OH)), 4.28 ppm (S, 2H, -CH_2-OH), 4.77 ppm (S, 2H, -CH_2O-(C=O)-).

^{1}H NMR of BPDE initiator: ^{1}H NMR ($CDCl_3$): 1.84 ppm (S, 12H, -C(Br)$(CH_3)_2$), 4.72 ppm (S, 4H, -CH_2O-(C=O)-).

2.4 Polymerization: Polymerization was carried out in a 50 mL Schlenk type reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr, bipyridine and a tiny magnetic capsule. Three cycles of vacuum-evacuation of reactor and fill-up with nitrogen gas were performed, and the reactor was then sealed with rubber septum. A required amount of degassed styrene and initiator (BPE or BPDE) were added with a syringe. The reactor was placed in an oil bath at the desired temperature controlled by a thermostat and the reaction mixture was stirred for certain time. At timed intervals, the polymerizations were stopped by addition of methanol followed by cooling the reactor into ice-water and the polymer was precipitated in methanol by stirring overnight. The polymers obtained were filtered, adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

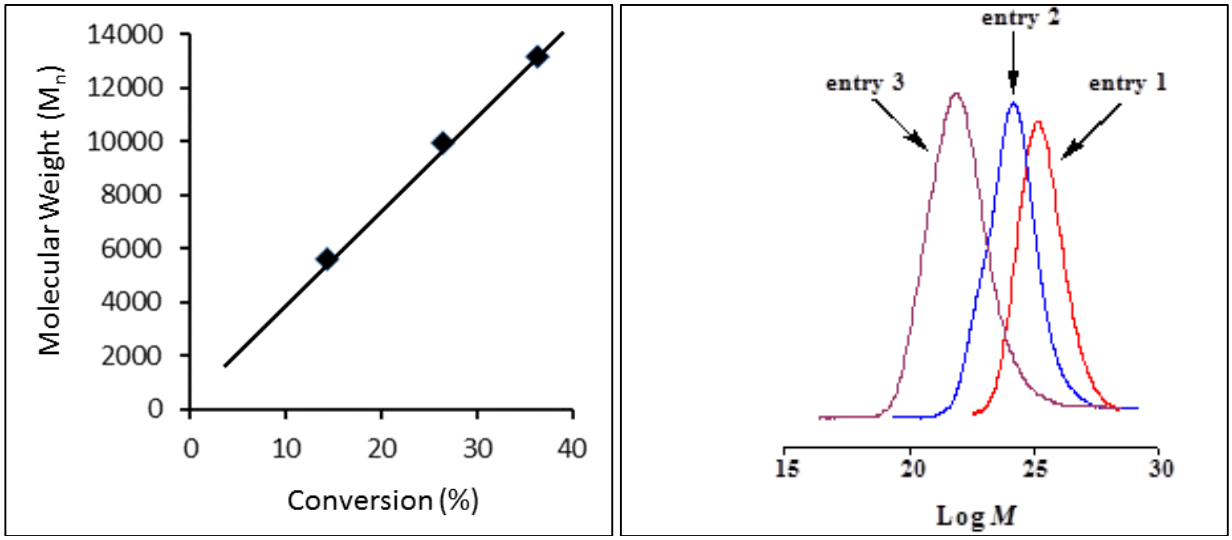
3. Result and Discussion

3.1 Polymerization of styrene by ATRP using BPE ester as an initiator: Styrene was polymerized by ATRP initiated by BPE at 115 ^{0}C using three different time duration in conjugation with copper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The results of the polymerization are shown in the Table 1. The molecular weight (M_n) of polymers affected with the polymerization time. The yield as well as molecular weight of the polymers was increased with increasing polymerization time. The GPC curves of polymers obtained were compared in Figure 1B. The GPC traces were shifted to the higher molecular weight region with increasing polymerization time maintaining narrow molecular weight distributions (Mw/Mn). The plot of M_n vs. conversion showed the linear relationship (Figure 1A) which indicated the living polymerization of styrene at 115 ^{0}C using CuCl/BiPy/BPE catalyst system.

Table 1: Effect of Time on Polymerization of Styrene using BPE as Initiator[a].

Entry	Time (hour)	Yield (gm)	M_n[b] (10^3)	M_w[c] (10^3)	M_w/M_n[d]	Conversion %
1	2	0.39	5604	6735	1.20	14.30
2	4	0.72	9944	11358	1.14	26.40
2	6	0.99	13161	16320	1.24	36.30

[a]polymerization conditions; CuBr : Bipy = 1:2, Styrene = 3.0 mL (26.8 mmol), temperature = 115 [o]C, [b]Number average molecular weight, [c]weight average molecular weight and [d]molecular weight distribution were measured by GPC analysis using polystyrene standard.



(A) **(B)**

Fig 1: Plot of conversion vs. molecular weight (A) and (B) GPC curves of the polymers.

3.2 Analysis of the structure of the polystyrene obtained by ATRP using BPE as an initiator: The structure of polystyrene obtained using BPE as initiator was investigated by the ^{1}H NMR analysis (Figure 2).

The -CH_3 protons (denoted bye in the structure) of BPE moiety in the polystyrene was observed at 1.54 ppm. The peaks observed at 4.25 ppm and 4.48 ppm (which were clearly seen in the expanded region) attributed to –CH_2- protons (denoted by b and c) of HO-CH_2-C≡C-CH_2-O- group of BPE moiety in the polymer chain end which indicated the presence of the BPE segment at end of the polymer chain. A broad peak observed at 4.50 ppm attributed to -CH proton (denoted by l) α- to Br. A broad signal observed at 7.0 ppm was assigned to aromatic protons (ortho- and meta- position) of styrene unit labeled as g and h and at 6.5 ppm for para-protons labeled as i in Figure 2. The signals observed at 1.48 ppm and 1.83 ppm were assigned for the -CH_2 and –CH protons of main chain of polystyrene labeled as c, c', d, d', e, e' etc respectively.

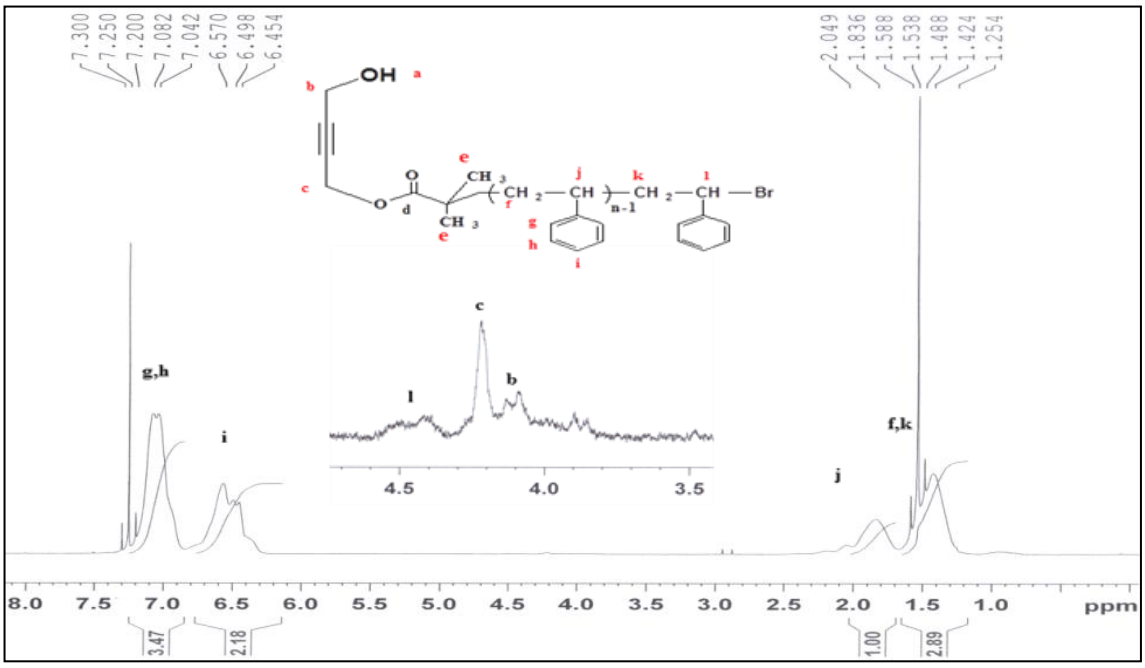


Fig 2: ^{1}H NMR spectra of the polystyrene obtained by using BPE.

3.3 Polymerization of styrene by ATRP using BPDE as initiator: BPDE initiated ATRP of styrene was conducted at 115 ^{0}C at three different time duration with copper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The results of the polymerization are shown in the Table 2. The yield and the molecular weight of polymers were affected with the polymerization time. Both the yield and molecular weight of the polymers were increased with increasing polymerization time. The GPC curves of polymers obtained were compared in Figure 3(B). The curves were shifted to the higher molecular weight region keeping narrow molecular weight distributions (M_w/M_n) with increasing polymerization time. The plot of molecular weight (M_n) vs. conversion (Figure 3A) showed linear increase of molecular weight of polymer with conversion. The above results indicated that the length of the polymer chain was controlled by changing the polymerization time in the polymerization of styrene using CuCl/BiPy/BPDE catalyst system.

Table 2. Effect of Time on Polymerization of Styrene using BPDE as Initiator[a].

Entry	Time (h)	Yield (g)	M_n[b] (10^3)	M_w[c] (10^3)	M_w/M_n[d]	Conversion %
1	0.5	0.52	5027	7324	1.45	19.11
2	1	0.90	11601	13271	1.14	33.08
3	2	1.22	14883	17548	1.18	44.85

[a]Polymerization conditions; CuBr : Bipy = 1 : 2, Styrene = 3.0 mL (26.8 mmol), temperature = 115 °C, [b]Number average molecular weight, [c]weight average molecular weight and [d]molecular weight distribution were measured by GPC analysis using polystyrene standard.

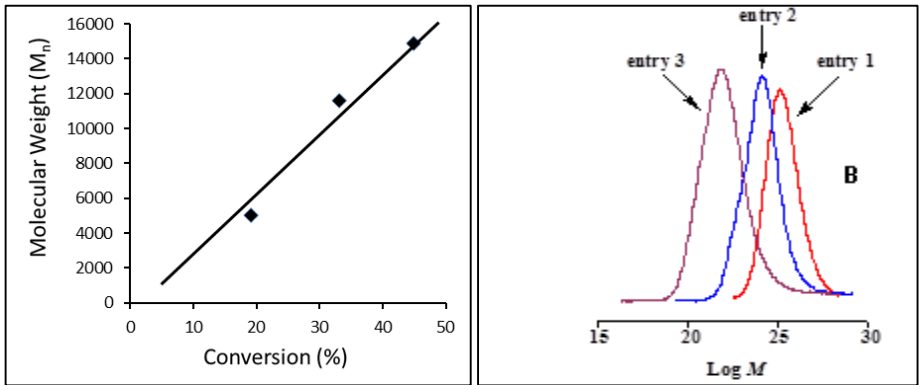


Fig 3: (A) Plot of molecular weight vs conversion and (B) GPC curves of the polymers.

3.4 Analysis of the structure of the polystyrene obtained: The structure of polystyrene obtained by using BPDE was investigated by the ^{1}H NMR analysis (Figure 4). The -CH_3 protons (denoted by b, b') of BPDE moiety in polystyrene at 1.54 ppm. The peak observed at 4.0 ppm attributed to the -CH_2- protons (denoted by a and a') of -O-CH_2-C-C-CH_2-O- group of BPDE moiety in the polymer chain (clearly observed in the expanded region of the spectrum) which indicated the presence of the BPDE segment at the polymer chain. A broad peak observed at 4.50 ppm attributed to CH proton (denoted by j, j') α- to Br of the polymer chain end. Two broad signals at 6.50 ppm and at 7.20 ppm were assigned to aromatic para-protons (labeled as m, m' in Figure 4) and aromatic ortho- and meta- protons (labeled as k, k' and l, l' in Figure 4) of styrene unit respectively. The signals observed at 1.48 ppm and 1.83 ppm were assigned for the -CH_2 and -CH protons of main chain of polystyrene labeled as c, c', d, d', e, e' etc respectively.

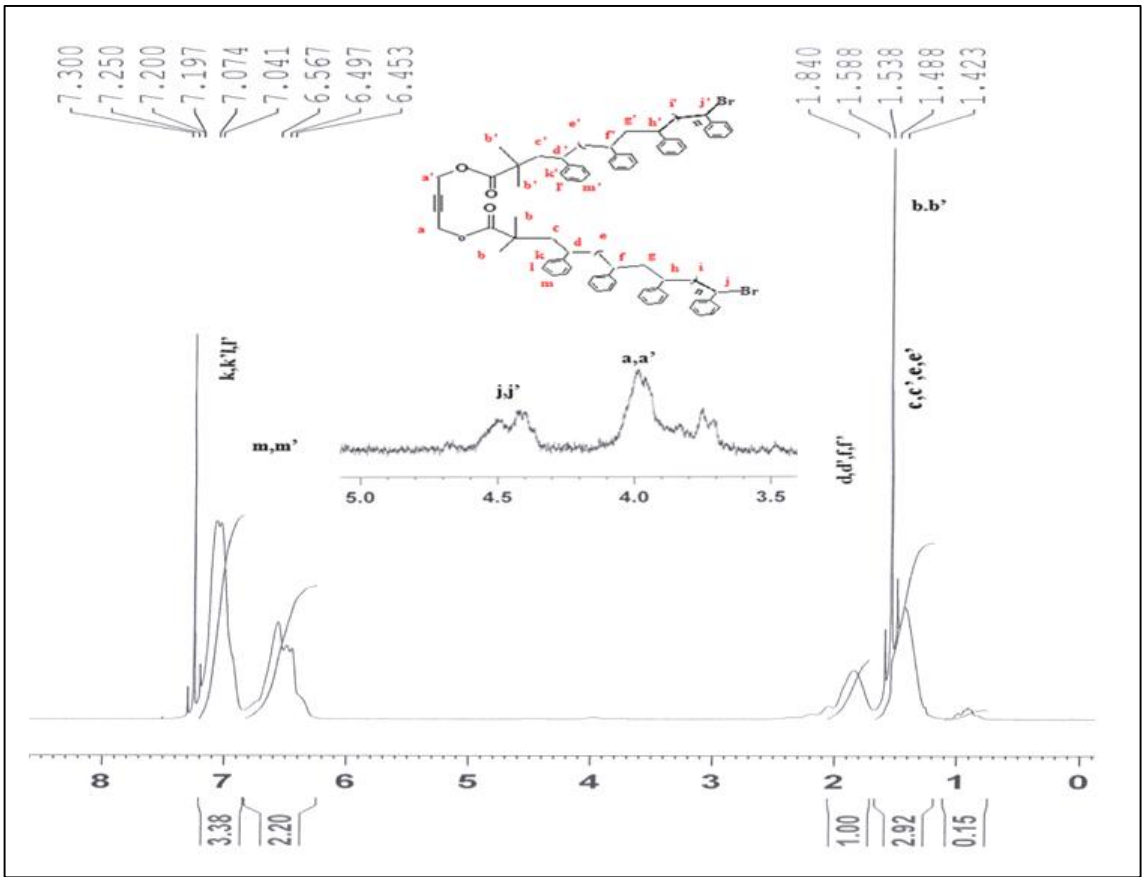


Fig 4: ^{1}H NMR spectrum of the polystyrene obtained by BPDE.

4. Conclusion

Internal and mid alkyne-functional polystyrenes were successfully synthesized by Atom Transfer Radical Polymerizations of styrene using BPE and BPDE initiators and Cu(I)/bipyridine catalyst at 115 ^{0}C. In both the catalyst systems, molecular weight of polymers was increased linearly with increasing the conversion keeping narrow molecular weight distribution. ^{1}H NMR analysis of polystyrene indicated that the internal and mid alkyne-functional polystyrenes were produced by BPE and BPDE initiators. These alkyne functional polystyrenes might be used as precursor for alkyne-azide cycloaddition click reaction.

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