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Synthesis of well-defined azido end-functional polystyrene: Monomer concentration and temperature effects on polymerization

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Abstract

Azide end-functional initiator 1-azidoethane-2-oxy-2-bromopropionyl (AEOBP) was synthesized by esterification of 2-azidoethanol and 2-bromopropionyl bromide in presence of triethylamine (Et_3N) in dry Tetrahydrofuran (THF). Azido end-functional polystyrene (PS- N_3) was synthesized by AEOBP initiated CuBr/bipyridine mediated Atom Transfer Radical Polymerization (ATRP) technique with controlled molecular weight and narrow polydispersity. The yield and molecular weight of polystyrene increased with increasing styrene/AEOBP ratio and reaction temperature. The structures of the polystyrene and AEOBP initiator were characterized by ^1H NMR spectra and the molecular weight of the polystyrene was determined by Gel Permeation Chromatography (GPC).

Keywords: End-functional polystyrene, Functional initiator, Atom transfer radical polymerization, Temperature effect on polymerization.

1. Introduction

Atom Transfer Radical Polymerization (ATRP) ^[1-4] is a Controlled or Living Radical Polymerization (CRP or LRP) technique and has been widely used for the synthesis of end-functional polymers/copolymers of various kind of monomers with precisely controlled architecture over different structures and compositions ^[4-9]. In ATRP system, all chain ends are retained and no new chain is formed. Thus chain end-functionality can be introduced into the polymer chain by regulating the structure of the functional initiator ^[10]. ATRP technique produces polymers with narrow molecular weight distributions, controlled molecular weights and high degree of chain end-functionality because of small amount of terminations. It has effectively been applied to the preparation of polymers with controlled functionalities, topologies and compositions ^[11, 12]. The number average molecular weight of the polymers prepared by ATRP depends on the ratio of initial concentration of monomer and initiator as well as the conversion of the monomer. The end-functional initiators play a significant role in ATRP to determine the number of initiated chains. With the use of a functional initiator, functionalities such as azide, vinyl, allyl, epoxide, cyano, hydroxyl and other groups are incorporated at one end of the chain, while the other end of the chain remains an alkyl halide ^[13, 14]. Reactive end group of a polymer chain has great potential for further modification of the polymer chains. Azido end of polymer chain reacts with alkyne group and gives cycloaddition using Click Reaction ^[15]. The copper-catalyzed Huisgen dipolar cycloaddition of a terminal alkyne and an azide ^[16, 17] have drawn much attention because of high efficiency, high specificity and technical simplicity. ATRP technique combined with Click Chemistry for the preparation of advanced macromolecular architectures ^[18] has a wide scope and large range of applications. In this point of view, well-defined azido end-functional polystyrene was synthesized by ATRP with different styrene/AEOBP ratio and reaction temperatures. The azido end-functional polystyrene could be used as a precursor for alkyne-azide click reaction to produce new macromolecules.

2. Materials and method

2.1. Materials

Styrene was purchased from Aldrich Co Ltd. It was purified by passing through an alumina column to remove stabilizer and then stirred with dry CaH_2 for 7 hr and filtered. Finally, it was stored at 0°C under N_2 gas before use. Copper (I) bromide, bipyridine and 2-bromopropionyl

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bromide were purchased from Sigma-Aldrich Co Ltd. 2-bromoethanol was purified under vacuum distillation. All solvents were purified by distillation followed by refluxing with Na and CaH₂.

2.2. Synthesis of 2-azidoethanol (2)

A mixture of NaN₃ (32.68 g, 502.7 mmol), 2-bromoethanol (21.5 mL, 303.5 mmol) and water (102 mL) was stirred for 12 hr at 80°C in a 250 mL round-bottom flask. The solution was cooled to room temperature and then extracted with ether (2.50 mL), dried with dry MgSO₄ and filtered. Solvent was removed from the filtrate under vacuum and a colorless liquid was obtained as product (85% yields).

2.3. Synthesis of 1-azidoethane-2-oxy-2-bromopropionyl (AEOBP)

In a 250 mL round-bottom flask, 2-azidoethanol (2.48 g, 28.5 mmol) and triethylamine (7.8 mL, 56 mmol) were dissolved in 45 mL of THF. The solution was cooled to 0°C with an ice-bath. 2-Bromopropionyl bromide (3.1 mL, 29.6 mmol) was added drop-wise and the mixture was stirred for 7 hr at room temperature. The product was extracted from ice-cold water with ether. The combined organic layer was washed sequentially with a saturated solution of Na₂CO₃, HCl solution (pH 4.5) and a second aliquot of Na₂CO₃. The organic layer was dried over MgSO₄ and concentrated in vacuo to yield yellow oil. Finally, the crude product was purified by silica gel column chromatography to yield a yellowish oil (yield 80%). The structure of the product was confirmed by ¹H NMR spectrum.

¹H NMR (solvent CDCl₃, δ in ppm): 4.25 (*t*, 2H, -CH₂-O-), 4.10 (*q*, 1H, -CH-Br), 2.81 (*d*, -CO-CH₂-CH-), 1.78 (*d*, 3H, -CH₃), 1.68 (*t*, 2H, -CH₂-N₃).

2.4. Polymerization of styrene by ATRP technique.

The polymerization of styrene was carried out at different ratios of styrene/AEOBP and different temperatures. A 25 mL Schleck flask was charged with required amount of dry CuBr and bipyridine. A required amount of degassed styrene and initiator were added with a syringe. The solution was degassed by three freeze-pump-thaw cycles, back filled with nitrogen, and then placed in an oil bath (preheated at the desired temperature) for different time intervals. The polymerization was quenched in MeOH. The crude polymers were dissolved in CHCl₃ and passed through an alumina plug to remove the metal/ligand catalyst system. The polymer solutions were concentrated and then precipitated in methanol. Finally the polymers were dried under vacuum at 60°C for 7 hr. The structure of the product was characterized by ¹H NMR spectrum analysis.

¹H NMR (solvent CDCl₃, δ in ppm): 4.38 (-CH₂-O-CO-), 3.78 (-CH (C₆H₅)-Br), 3.21 (-CO-CH-CH₃), 1.73 {*b*, -CH₂-CH (C₆H₅)- and (-CH₂-N₃)}, 1.36 {*b*, -CH₂-CH (C₆H₅)- and -CH-CH₃}, 7.10 {*b*, (*o*, *m*) C₆H₅-}, 6.50 {*b*, (*p*) C₆H₅-}.

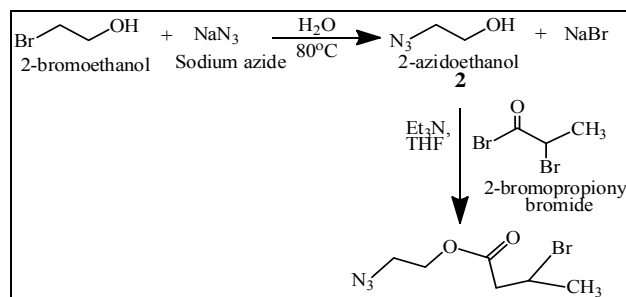
2.5. Analytical method

Molecular weight (*M_w*) and molecular weight distribution (*M_w/M_n*) of polymer were measured by Toyo Soda HLC-802; Column GMH6×2+G40000H8; eluent, CDCl₃ as solvent and calibrated by polystyrene standards. ¹H NMR spectra of polymers were recorded at room temperature on a BRUKER 500 spectrometer operated at 500 MHz in pulse Fourier transform mode with chloroform-d as solvent. The peak of chloroform-d (7.25 ppm) was used as internal reference.

3. Results and discussion

3.1. Chemical reactions and structural characterization

1-azidoethane-2-oxy-2-bromopropionyl (AEOBP) initiator was prepared starting from 2-bromoethanol following reaction Scheme 1. 2-azidoethanol was obtained from 2-bromoethanol by a simple substitution reaction with sodium azide. The esterification of 2-azidoethanol was then treated with 2-bromopropionyl bromide to produce 1-azidoethane-2-oxy-2-bromopropionyl (AEOBP) initiator. The chemical reactions involved in the formation of AEOBP was given in Scheme 1.

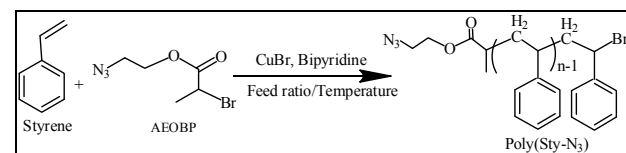


1-Azidoethane-2-oxy-2-bromopropionyl (AEOBP)

Scheme 1: Synthesis of AEOBP.

The structure of 1-azidoethane-2-oxy-2-bromopropionyl was confirmed by ¹H NMR spectroscopy. ¹H NMR spectrum of AEOBP showed a broad quartet peak centered at 4.10 ppm was assigned to be -CH (Br) proton and a doublet appeared at 1.78 ppm was assigned to -CH₃ protons. The presence of these two signals indicated the propionyl part in the product. A triplet at 4.25 ppm was appeared for -CH₂-CH₂-O- and another triplet at 2.81 ppm for N₃-CH₂-CH₂-O- protons were also assigned.

The AEOBP was used as initiator and was successfully applied with Cu (I)-bipyridine mediated ATRP to prepare azido end-functional polystyrene at different reaction conditions such as, various feed ratios of monomer and different reaction temperatures (Scheme 2).



Scheme 2: Synthesis of Azido end-functional polystyrene.

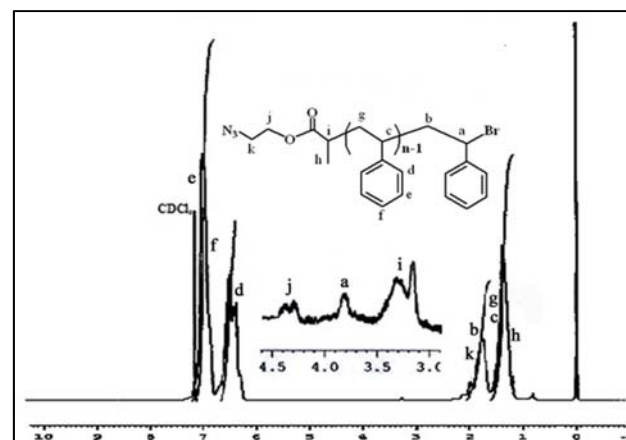


Fig 1: ¹H NMR spectrum of azido end-functional polystyrene.

¹H NMR spectrum of this compound confirmed the structure of azido end-functional polystyrene. In the spectrum (Fig.1), the signals appeared at 4.38 and 3.78 ppm were assigned to be -CH₂-O-CO- and -CH-(C₆H₅)-Br protons (denoted by j and a), respectively. Peak appeared at 3.21 could be assigned to -CO-CH-CH₃ proton (denoted by i). A broad signals appeared at 1.73 were assignable to -CH₂-CH (C₆H₅) - and -CH₂-N₃ protons (b and k). Another broad peak at around 1.36 was assignable to -CH₂-CH (C₆H₅) - and -CH-CH₃ protons (h and g). This result indicated that the polymerization was initiated with AEOBP initiator. A broad signal appeared at around 7.10 ppm was assigned to be aromatic protons (meta- and ortho-position) of styrene unit (D and E) and another broad signal at around 6.5 ppm was assigned to protons of the para-position (F).

3.2. Effect of temperature on polymerization

The effect of temperature on the polymerization of styrene with AEOBP/CuBr/Bipyridine (1:1:2.1) was determined at three different temperatures (100, 115 and 130°C) under the same reaction conditions. The results obtained were listed in Table 1.

Table 1: Effect of the temperature on polymerization of styrene^a

Entry	Temp (°C)	Yield (g)	^b M _n (×10 ³)	^c M _w (×10 ³)	^d M _w /M _n
4	100	trace	-	-	-
5	115	0.50	40.1	68.3	1.70
6	130	1.29	54.5	83.4	1.53

^aPolymerization conditions; CuBr = 0.027 mmol, Bipyridine = 0.056 mmol, styrene = 3 mL (26.18 mmol), styrene/ AEOBP = 1000, time = 5 hrs. ^bNumber average molecular weight, ^cweight average molecular weight and ^d molecular weight distributions were measured by GPC analysis using polystyrene standard.

A trace amount of polymer was obtained at 100°C, whereas the yield of polymers was increased with higher reaction temperature at 115°C and 130°C. The GPC curves of the polymers obtained were shown in Fig. 3.

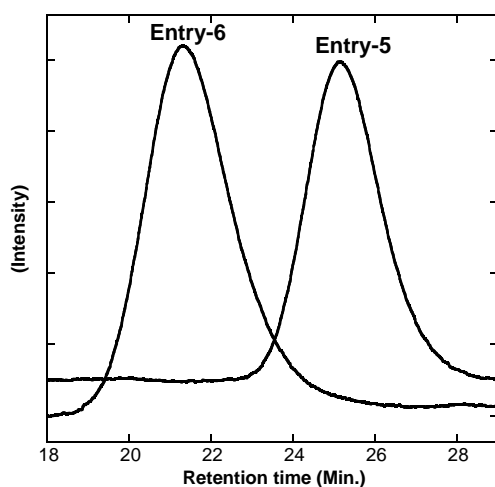


Fig 2: GPC curves of entry 5 and entry 6.

The polymer with higher molecular-weight was obtained at 115°C and 130°C. With increasing temperature the molecular weight of the polymers was increased while the molecular weight distribution became narrower. These results indicated that the initiation and propagation rate were increased with increasing the reaction temperature.

3.3. Effect of different ratio of styrene and initiator on polymerization

Styrene was polymerized by ATRP technique at 115°C using three different ratios of styrene and initiator (St/AEOBP = 250, 500 and 1000) together with Cu (I) Br-Bipyridine catalyst system under nitrogen atmosphere. The results of the polymerization are listed in Table 2. The catalytic system gave polymer with high molecular weight and narrow molecular weight distribution.

Table 2: Effect of different ratio of styrene/initiator on polymerization of styrene^a

Entry	Styrene/ AEOBP (mmol)	Yield (g)	^b M _n (×10 ³)	^c M _w (×10 ³)	^d M _w /M _n
1	250	0.25	7.3	9.7	1.33
2	500	0.45	15.6	21.0	1.34
3	1000	0.76	40.1	68.3	1.70

^aPolymerization conditions; styrene = 3 mL (26.18 mmol), CuBr: Bipyridine = 1:2, temperature = 115°C, time = 5 hr. ^bNumber average molecular weight, ^cweight average molecular weight and ^dmolecular weight distributions were measured by GPC analysis using polystyrene standard.

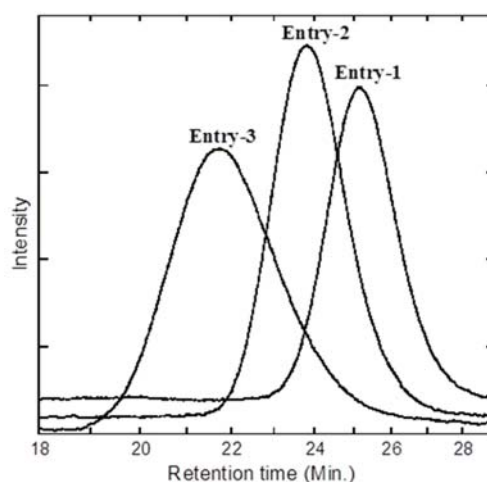


Fig 3: GPC curves of entry-1, entry-2 and entry-3.

The GPC curves of the polystyrene obtained are shown in Fig. 3. The GPC curve of the polymers was shifted to higher molecular weight region with increasing the monomer/initiator feed ratio while the molecular weight distribution became narrower. As shown in Table 2, narrower (M_w/M_n = 1.33) molecular weight distribution of the polymer was obtained with lower ratio of monomer and initiator in entry 1 and comparatively broader distribution (M_w/M_n = 1.70) was obtained with that of higher ratio in entry 3.

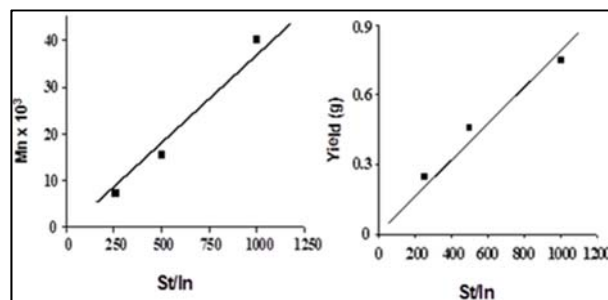


Fig 4a: Plot of M_n vs St/AEOBP **Fig 4b:** Plot of yield vs St/AEOBP

The yield and number average molecular weight (M_n) of the polymers were linearly increased with increasing the ratio of St/AEOBP (Fig. 4a and 4b). These results suggested that the propagation rate was proportionally increased with increasing monomer feed.

Conclusions

The initiator 1-azidoethane-2-oxy-2-bromo propionyl (AEOBP) was synthesized with good yield. The structure of AEOBP was confirmed by ^1H NMR spectrum. The synthesized AEOBP was used as initiator and successfully applied with Cu (I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was carried out at various reaction conditions. A trace amount of polymer was obtained at 100 °C. On the other hand, a good amount of polymer was obtained at 115 °C and 130 °C. The yield and molecular weight of polymers were obtained to be increased with increasing the temperature. This result suggested that the efficiency of AEOBP as initiator for ATRP of styrene was good enough at above 115 °C.

The yield and the molecular weight of polymers were increased with increasing the feed ratio of styrene. This result suggested that the propagation rate was increased with increasing monomer concentration. The azido end-functional polystyrene synthesis in this research could be used as a macromolecular precursor for Click Reaction.

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