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End-functionalization of azide (N_3)-terminated polystyrene with different functional groups

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Abstract

Azide (N_3)-terminated polystyrene ($M_n = 15,600$ g/mol, $M_w/M_n = 1.34$) have been successfully converted into four different end-functionalized (bromide-, chloroacetate-, hydroxyacetate-triazole- and amino-terminated) polystyrenes by Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) mediated Click Reaction and proper chemical transformation. All the desired products were obtained in high purity and with good yield. The structure of the synthesized polystyrenes have been confirmed by 1H NMR spectral analysis.

Keywords: Azide (N_3)-terminated polystyrene, End-functionalized polystyrene, Atom transfer radical polymerization (ATRP), Triazole ring

1. Introduction

An efficient modification reaction with high selectivity is important to develop new polymeric materials for macromolecular engineering and biological applications. The term 'Click Chemistry' is a broad class of reactions, which is versatile, fast, simple to use, easy to purify and give high yield has been extensively used as a technique for polymer modification [1, 2]. This reaction can be applied to many multitude macromolecular transformations [3-9], among which 1,3-dipolar azide-alkyne cycloaddition [10] has received significant attention as it can be regioselectively catalyzed by Cu^I to produce 1,4-triazoles at room temperature. The Cu^I -catalyzed Click Reaction has been applied widely in polymer and materials science [11, 12]. Usually the Cu^I -catalyzed azide-alkyne cycloaddition is applied to terminal alkynes, but selecting appropriate catalyst [13] it can be extended to internal alkynes.

The application of Click Chemistry together with Controlled Radical Polymerization (CRP) has contributed to rapid development in the available range of polymer architectures and functional materials because of the ease of combination of two synthetic techniques. The majority of polymers functionalized using the CuI -catalyzed azide-alkyne cycloaddition has been prepared by ATRP. There are a variety of available methods for incorporating clickable groups into a polymer chain, including the use of functional monomers or initiators and post polymerization modification reactions. The halogen end groups of polymers prepared by ATRP are easily converted to azido moieties by simple nucleophilic substitution [14].

End-functionalized polymers are industrially important pre-polymers for making block, graft co-polymers and cross-linked polymers with network structures. End-functionalized polymers plays an important role in the polymer's ultimate property and allow the polymer to couple with other functionalities forming grafts or blocks, cross-linking. The ω -end, being living, can further chain extend, thereby allowing the formation of functional blocks. Control over the synthesis of blocks, grafts architectures has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving or expressing particular polymer properties by self-assembly.

We have synthesis well-defined azido end-functional polystyrene by ATRP technique which has been reported in our recent publication [15]. In the present study, the azide (N_3)-terminated polystyrene has been converted to triazole ring containing bromide (-Br), chloroacetate ($ClCH_2COO-$), hydroxyacetate ($HOCH_2COO-$) end-functionalized polystyrenes by CuI -catalyzed Azide-Alkyne Cycloaddition (CuAAC) mediated Click Reaction and amino ($-NH_2$)-terminated polystyrene by chemical transformation.

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2. Materials and Method

2.1. Materials

The azide (N_3) end-functional polystyrene was synthesized by ATRP method starting with 2-bromoethanol and sodium azide. Details of this synthesis has been reported in our recent paper [15]. This polymer was purified by dissolving in $CHCl_3$ and passing through an alumina column. It was then dried and finally precipitated in MeOH.

All chemicals were purchased from Sigma-Aldrich Co Ltd. Copper iodide was purified by recrystallization in H_2O and washed with EtOH, ether, ethyl acetate and n-hexane successively. Propargyl bromide was purified by reduced pressure distillation. KOH pellets was purified by reduced pressure distillation. 2-Chloroacetic acid was crystallized from $CHCl_3$, dried and stored under dry N_2 gas. Triphenyl phosphine was purified in hot ethanol. All solvent were purified by distillation followed by refluxed with Na and dry CaH_2 .

2.2. Synthesis of bromide-triazole terminated polystyrene (2)

To a 100 mL R. B. flask, 0.7 g of azidoe (N_3) end-functional polystyrene (1) ($M_n = 15,600$ g/mol, $M_w/M_n = 1.34$) was dissolved in chloroform (7 mL) and, 0.2 g of CuI and 80 mg (0.68 mmol) of propargyl bromide were added to this solution. The mixture was degassed by bubbling N_2 gas for 15 min and stirred at room temperature overnight. The catalyst (CuI) was removed by filtration. The product was extracted with CH_2Cl_2 and washed two times with 20 mL of 25 % NH_4OH solution and finally it was washed 3 times with 30 mL of water. The crude product was precipitated in MeOH. The product was filtered and dried. Then it was dissolved in $CHCl_3$ and the solution was passed through the alumina column for purification. The eluent was poured in MeOH with stirring to precipitate the polymer. The desired product was filtered and dried under vacuum at 60 °C. The yield of product was 90%.

1H NMR (solvent $CDCl_3$, δ in ppm): 1.36 (-CO-CH- CH_3), 1.52 {- CH_2 -CH (C_6H_5)}, 1.82 {- CH_2 -CH (C_6H_5)}, 3.21 (-CO-CH- CH_3), 3.80 (- CH_2 - N_3), 3.88 {-CH (C_6H_5)-Br}, 4.45 (- CH_2 -O-CO-), 5.15 (- CH_2 -Br), 6.60 {(*p*) C_6H_5 -}, 7.10 {(*o*, *m*) C_6H_5 -}, } and 7.85 (triazole proton).

2.3. Synthesis of chloroacetate-triazole terminated polystyrene (3)

2.3.1. Synthesis of α -chloro propargyl acetate

3.1 g (32.80 mmol) of chloroacetic acid and 2.02 g (36.08 mmol) of KOH pellets were dissolved in 15 mL of DMF in a 250 mL R.B. flask. The mixture was stirred at 100 °C for 1.5 hrs. Then 2.74 mL (36.08 mmol) of propargyl bromide was added drop-wise to this solution for 25 min and then the mixture was stirred and allowed to react at 70 °C for 17 hrs. The reaction mixture was cooled at room temperature, filtered and dried. The residue was dissolved in 30 mL of distilled water and extracted with 25 mL of CH_2Cl_2 . The solvent was removed under vacuum. The product was purified by short column using petroleum ether: ethyl acetate (90:10) as eluent. The yield of the product was obtained to be 70 %.

2.3.2. Synthesis of chloroacetate-triazole terminated polystyrene using α -chloropropargylacetate

To a 25 mL of Schlenk tube, 0.2 g of azide (N_3) end-functional polystyrene ($M_n = 7,300$ g/mol) was dissolved in

$CHCl_3$ (5 mL), then 0.52 mg of CuI catalyst and 7.26 mg (0.054 mmol) of α -chloropropargylacetate were added to this solution. The reaction mixture was degassed by bubbling N_2 gas for 12 min and stirred at room temperature overnight. CuI was removed by filtration. The filtrate was diluted with $CHCl_3$ and washed with 5 mL of NH_4OH (25% solution in H_2O) and 20 mL of water 3 times successively. Dry $MgSO_4$ was added to the solution and it was kept at room temperature for overnight and filtered. The filtrate was concentrated under vacuum and precipitated in MeOH, filtered and dried under vacuum at 60 °C. Finally, the polymer was washed with CH_2Cl_2 and dried. About 73% yield of this product was obtained.

1H NMR (solvent $CDCl_3$, δ in ppm): 1.37 (-CO-CH- CH_3), 1.50 {- CH_2 -CH (C_6H_5 -)}, 1.82 {- CH_2 -CH (C_6H_5 -)}, 3.24 (-CO-CH- CH_3), 3.81 (> N - CH_2 -), 3.88 (-CH (C_6H_5)-Br), 4.45 (- CH_2 -O-CO-), 4.64 (- CH_2 -Cl), 5.46 (-O- CH_2 -C), 6.61 {(*p*) C_6H_5 }, 7.11 {(*o*, *m*) C_6H_5 } and 7.83 (triazole proton).

2.3. Synthesis of hydroxyacetate-triazole terminated polystyrene (4)

In a 25 mL of Schlenk tube, 0.05 g of chloroacetate-triazole terminated polystyrene (3) was added to 4 mL of THF, 7 drops of water and 0.754 mg (0.013 mmol) of KOH pellets were added to this mixture. The reaction mixture was stirred for 2 hrs at 80 °C and then for 8 hrs at room temperature. The solution was concentrated and diluted in $CHCl_3$ and washed with water. The organic layer was precipitated in MeOH by passing through a neutral alumina column. The yield of product was obtained to be 84%.

1H NMR (solvent $CDCl_3$, δ in ppm): 1.37 (-CO-CH- CH_3), 1.52 {- CH_2 -CH (C_6H_5 -)}, 1.83 {- CH_2 -CH (C_6H_5)}, 3.25 (-CO-CH- CH_3), 3.65 (-OH), 3.80 (- CH_2 - N_3), 3.87 {-CH (C_6H_5)-Br}, 4.47 (- CH_2 -O-CO-), 4.74 (- CH_2 -OH), 5.44 (-O- CH_2 - N_3), 6.60 {(*p*) C_6H_5 }, 7.12 {(*o*, *m*) C_6H_5 -} and 7.83 (triazole proton).

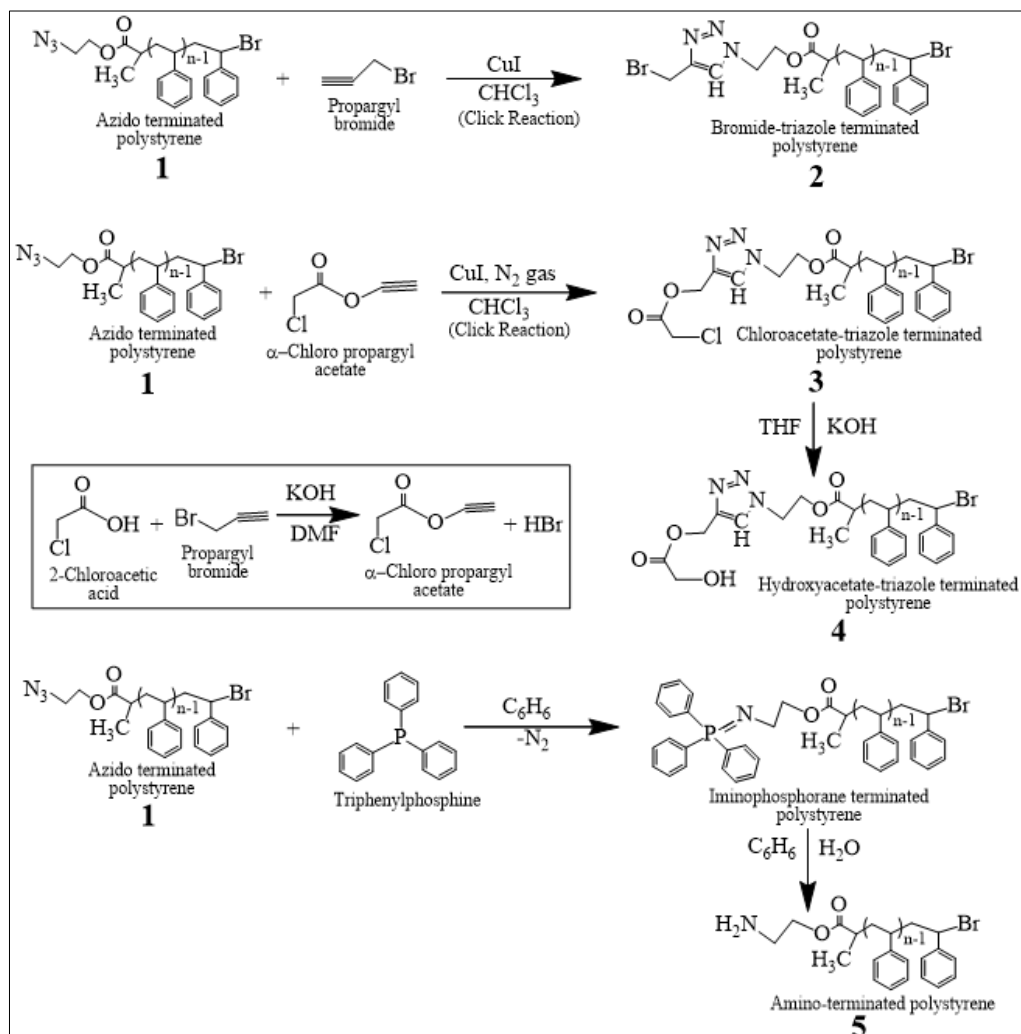
2.5. Synthesis of amino-terminated polystyrene (5)

To a 25 mL of Schlenk tube, 0.2 g of azide (N_3)-terminated polystyrene ($M_n = 7,300$ g/mol) and 0.02 g (0.08 mmol) of PPh_3 were dissolved in benzene. The solution was stirred at room temperature overnight. 2 mL of water was added to the mixture and then stirred at room temperature overnight. The upper layer was separated by a separating funnel and precipitated in MeOH by passing through the alumina column, filtered and dried. Finally, the solid was washed with hot ethanol and dried. The yield of product was about 90 %.

1H NMR (solvent $CDCl_3$, δ in ppm): 1.36 (-CO-CH- CH_3), 1.51 (- CH_2 -CH (C_6H_5)), 1.80 {- CH_2 -CH (C_6H_5)}, 3.13 (- CH_2 - NH_2), 3.24 (-CO-CH- CH_3), 3.88 {-CH (C_6H_5)-Br}, 4.45 (- CH_2 -O-CO-), 5.15 (- NH_2), 6.60 {(*p*) C_6H_5 -}, and 7.10 {(*o*, *m*) C_6H_5 -}.

3. Results and Discussion

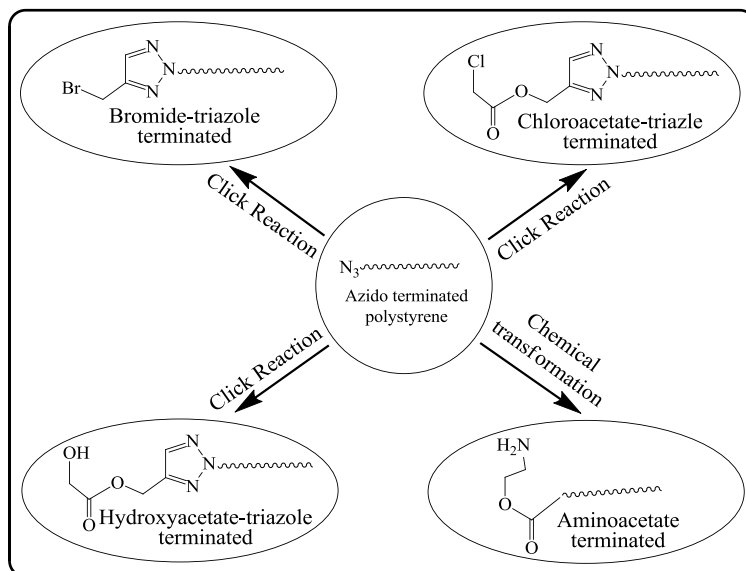
The synthesis of azide (N_3) end-functional polystyrene (1) was carried out starting from 2-bromoethanol and sodium azide. Details of synthesis of this polystyrene (1) and its characterization have been reported in our recent publication [15]. The bromide-triazole terminated polystyrene (2) was synthesized by Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) mediated Click Reaction from the azidie (N_3) end-functional polystyrene (1) and propargyl bromide in $CHCl_3$ solvent (Scheme 1 and 2).



Scheme 1. Conversion of azido group into bromide-triazole ring, chloro- and hydroxyl-acetate triazole ring and amino terminated polystyrene.

The structure of bromide-triazole terminated polystyrene (2) was characterized by ¹H NMR spectral analysis. In the ¹H NMR spectrum, signal appeared at 5.15 ppm assignable to -CH₂-Br protons and a signal appeared at 7.85 ppm assignable to triazole ring proton of ω -end of the chain were observed. The presence of triazole ring proton in the ¹H NMR spectrum indicated that the triazole ring was formed by CuAAC Click Reaction between azide group of pre-polymer and propargyl

bromide. A signal at 4.45 assignable to -CH₂-O-CO- protons and a signal at 3.80 assignable to triazole ring connected >N-CH₂- protons were observed. A signal at 3.88 assignable to -CH-Br proton of α - to Br were appeared in the spectrum. The peaks appeared at 1.36 and 3.21 were assigned to -CO-CH-CH₃ and -CO-CH-CH₃ protons, respectively. A broad signal at 7.10 and 6.60 were assigned to aromatic (*m*- and *o*-position) and (*p*-position) protons, respectively. The signals observed at 1.82 and 1.52 were assigned for the CH₂ and CH protons of the main chain of polystyrene, respectively.



Scheme 2. Functionalization of azide (N_3)-terminated polystyrene by CuAAC mediated Click Reaction and proper chemical transformation (only reaction part of the transformations are shown).

For the synthesis of chloroacetate-triazole terminated polystyrene (3), the starting material α -chloropropargyl acetate was obtained from 2-chloroacetic acid and propargyl bromide in presence of KOH pellets in DMF (inside rectangular box in Scheme 1). The triazole ring containing chloroacetate group was formed by CuAAC mediated Click Reaction between azido terminated polystyrene and chloropropargyl acetate in $CHCl_3$ solvent. The hydroxyacetate-triazole terminated polystyrene (4) was obtained by hydrolysis of chloroacetate-triazole terminated polystyrene (3) with KOH in THF solvent.

The structure of chloroacetate-triazole terminated polystyrene (3) was confirmed by 1H NMR spectrum. The signals appeared at 4.64 ppm and 5.46 ppm in the 1H NMR were assigned to $-CH_2-Cl$ and $-O-CH_2-C$ protons, respectively. A signal at 7.83 assignable to a triazole ring proton of ω -end of the chain was observed. The presence of triazole ring proton in the 1H NMR spectrum indicated that the CuAAC mediated Click Reaction between azide group of pre-polymer and alkyne group of chloropropargyl acetate was occurred successfully. A signal at 4.45 and 3.81 were assigned to $-CH_2-O-CO-$ and triazole ring connected $>N-CH_2-$ protons, respectively. Other signals corresponding to the main chain were also observed as follows: a signal at 3.88 assignable to CH proton α - to Br, a broad signal at 7.11 was assigned to aromatic protons (*m*- and *o*- position) of styrene unit and at 6.61 for *p*-proton, signals at 1.37 and 3.24 were assigned to $-CO-CH-CH_3$ and $-CO-CH-CH_3$ protons, respectively. The signals at 1.50 and 1.82 were assigned to the CH and CH_2 protons of the styrene unit, respectively.

The structure of hydroxyacetate-triazole terminated polystyrene (4) was also characterized by 1H NMR spectrum. Peaks similar to polystyrene (3) were observed in the 1H NMR spectrum for polystyrene (4). An additional peak appeared at 3.65 assignable to $-OH$ proton confirmed the transformation of chlorine atom into hydroxyl group.

The 1H NMR spectrum also confirmed the structure of amino-terminated polystyrene (5). All peaks in the 1H NMR spectrum of polystyrene (5) were similar to polystyrene (2) with exception of disappearing the peak at around 7.85 and an additional peak appeared at 5.15. The disappearance of peak

around 7.85 and appearance of peak at 5.15 confirmed that triazole ring transformed into $-NH_2$ group.

4. Conclusion

We have introduced various functional groups ($-Br$, $-Cl$, $-OH$, $-NH_2$) at the ω -end of azide (N_3) terminated polystyrene by using Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) mediated Click Reaction and proper chemical transformation. The post functionalization of azide (N_3) end-functional polystyrene into bromide-, chloroacetate- and hydroxyacetate-triazole terminated polystyrenes were successfully performed by CuAAC. The azide (N_3) terminated polystyrene was converted to aminoacetate terminated polystyrene by chemical transformation. All the polystyrenes were obtained in high purity and with good yield without causing significant change of molecular weight distribution. The structure of all the synthesized end-functionalized polystyrenes were confirmed by 1H NMR spectral analysis. These end-functionalized polystyrenes could be used as a precursor for various chemical reactions to produce new macromolecules.

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