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Synthesis and Characterization of Mono and Di arm α-halo esters as a Initiator for Atom Transfer Radical Polymerization

Kabir Homayun, Chowdhury Samiul Islam and Hasan Tariqul
Department of Chemistry, University of Rajshahi, Rajshahi-6205, BANGLADESH

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Abstract

2-Bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester (BPE) and 2-Bromo-2-methyl-propionic acid but-2-ynyl diester (BPDE) were synthesized by one step reaction which involved on esterification of 2-Bromo-2-methylpropionyl bromide with 2-Butyn-1,4-diol. Both the products were separated from the reaction mixture by (silica gel) column chromatography (EtOAc/petroleum ether = 1:50) and were obtained as yellowish liquid. *^{1}H NMR analysis confirmed the structure of BPE and BPDE. These two functional bromoesters could be used as initiator on Atom transfer radical polymerization (ATRP) to produce well defined functional polymers.*

Keywords: Atom transfer, ATRP, Initiator, polymerization.

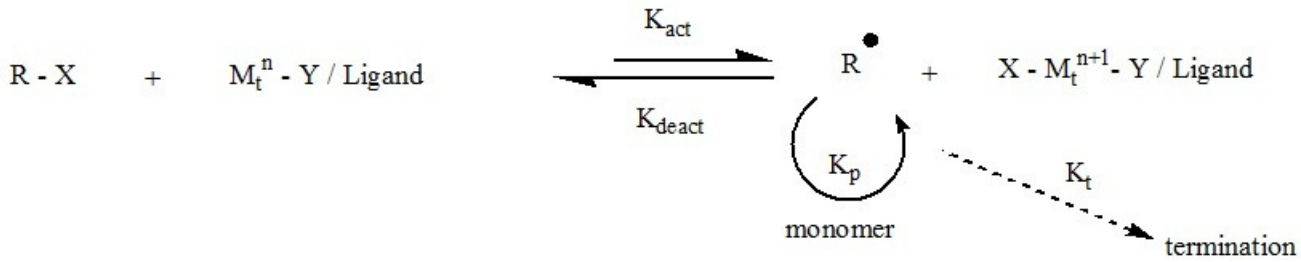
Introduction

Well-defined functional polymers are most important materials due to their application in chemistry, physics, medicine, biology and nanotechnology. Conventional free radical polymerization techniques are not able to produce polymers with well-defined or controlled molecular weights and molecular weight distributions due to large amount of chain transfer and termination reactions. Atom Transfer Radical Polymerization (ATRP), a polymerization technique combined with a suitable initiator has overcome these drawbacks[1-2].

Since its inception, ATRP also known as transition metal mediated living radical polymerization has proven to be robust for the design of polymers of complex architecture and precise molar mass.[3-5] ATRP tolerates many functional groups present in monomers or solvents, impurities present in solvents and monomers and also allows for the facile synthesis of many polymers of novel structure and topology[6].

ATRP generate of radicals (active species) through a reversible redox process catalyzed by a transition metal complex (M_t^n-Y / Ligand), which undergoes a one electron oxidation with concomitant abstraction of a halogen atom (X) from an initiator (R-X). Polymer chains grow by the addition of intermediate radicals to monomers according to radical polymerization. A very negligible amount of termination reaction (k_t) occurs in ATRP.[7] When the concentration of propagating radicals is very low, the proportion of terminated chain can be neglected. This may enable to produce functional polymers.

ATRP is a multicomponent system which includes monomer, initiator, catalyst, solvent and temperature. By using various functional initiators, different functional end group can easily be incorporated in the linear polymer chain. Alkyl halides (RX) or functional alkylhalides or functional haloesters are mostly used as ATRP initiators. After initiation, the initiator fragment R is present at the one end of the polymer chain while the halogen at the other end. Both ends can be further convert to other functionalities by means of suitable organic reaction. Terminal alkyne functional R fragment at the end of the polymer chain can be modified via click chemistry (alkyne-azide cyclization) to give telethelic, block and graft polymers[8-12]. Despite the examples for termenal alkyne-azide click cyclization are available, the mid alkyne-azide click cyclization is rare.



Scheme-1
Mechanism of metal complex-mediated ATRP

The mid alkyne-azide clicks cyclization using cyclopentadienyl based Ru catalyst[13]. Mid alkyne-azide click cyclization facilitate the synthesis of star type polymer. On the above point of view a terminal alkyne functional initiator 2-Bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester (BPE) and a mid alkyne functional initiator 2-Bromo-2-methyl-propionic acid but-2-ynyl diester (BPDE) initiators were synthesized in this study.

Material and Methods

Materials: 2-Bromo-2-methyl-propionylbromide was purchased from Sigma Aldrich and used without further purification. Pyridine was purified by distillation followed by stirring with CaH_2 for 24 hrs. 2-Butyn-1, 4-diol was purchased from Fluka. The solvents were used as received.

Analytical Methods: ^{1}H NMR spectra of polymers were recorded at room temperature on a JEOL GX 500 spectrometer operated at 400 MHz in pulse Fourier transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ^{1}H) was used as internal reference.

Synthesis of Alkyne End- and Mid- functional Bromoesters: 2-Butyn-1,4-diol (6.36 gm, 73.84 mmol) was dissolved in CH_2Cl_2 (15 mL). Dried pyridine (8.10 gm, 102.33 mmol) was added to the solution of 2-Butyn-1,4-diol. The mixture was then cooled to 0^0C. To the mixture 2-Bromo-2-methyl propionyl bromide (16.98 gm, 73.84 mmol) was added by using syringe. The reaction mixture was stirred for 48 hrs at room temperature using magnetic stirrer. The aqueous layer was extracted with CH_2Cl_2 (3×50 mL), then washed with water (50 mL), dried with $MgSO_4$, filtered and concentrated in vacuum. The residue was separated by (silica gel) column chromatography (EtOAc/ Petroleum ether = 1:50) and two products were isolated as yellowish liquid. The purity of the separated products was investigated by TLC using same solvent mixture. The expected products 2-Bromo-2-methyl-propionic acid but-2-ynyl diester (BPDE) (4.23 gm) and 2-Bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester (BPE) (2.72 gm) were obtained as yellowish liquid followed by evaporation of solvent from each eluent under vacuum. Finally, the structure of the products, BPDE and BPE were confirmed by ^{1}H NMR analysis.

^{1}H NMR of BPE ($CDCl_3$): 1.85 ppm (S, 6H, -C(Br)(C**H**$_3$)$_2$, at 3.84 ppm (broad , 1H, -O**H**)), 4.28 ppm (S , 2H, -C**H**$_2$-OH), 4.77 ppm (S, 2H, -C**H**$_2$O-(C=O)-).

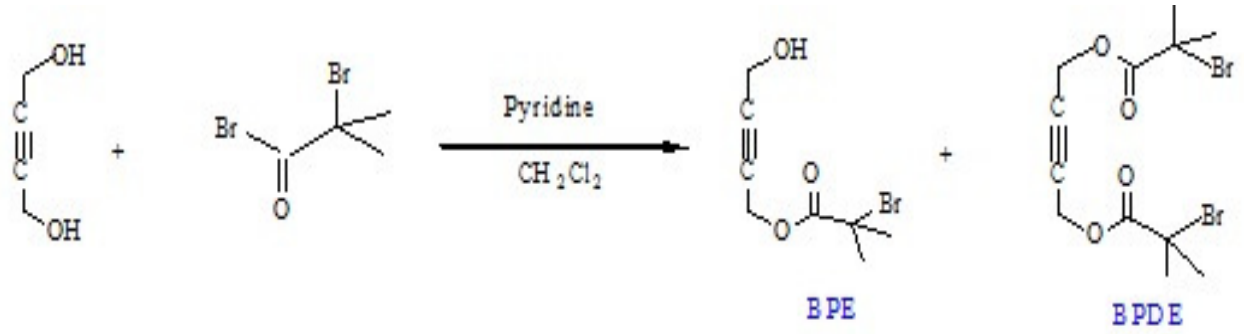
^{1}H NMR of BPDE ($CDCl_3$): 1.84 ppm (S, 12H, -C(Br)(C**H**$_3$)$_2$), 4.72 ppm (S, 4H, -C**H**$_2$O-(C=O)-).

Results and Discussion

The expected initiators BPE and BPDE, were synthesized from the reaction between 2-Butyn-1,4-diol and 2-Bromo-2-methyl propionyl bromide in the presence of pyridine and methylene chloride as following scheme 2. The structure of the initiator BPE and BPDE obtained were characterized by ^{1}H NMR analysis. In the ^{1}H NMR spectrum of the initiators, several signals including the signals of 2-bromo-2-methyl propionyl bromide were observed. All signals correspond to the different protons of BPE and BPDE was assigned clearly and labeled in figure-1 and figure-2.

The ^{1}H NMR spectrum of 2-Bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester (BPE), was displayed in figure-1. In the ^{1}H NMR spectrum, three singlets appeared at 1.85 ppm , 4.72 ppm, 4.28 ppm for -C(Br)$(CH_3)_2$, -CH_2O-(C=O)- 2H, -CH_2-OH protons denoted by d, c, b and a broad peak appeared at 3.84 ppm for –OH protons denoted by a respectively. The presence of two additional weak peaks with main peak suggested the presence of the conformers of this product. All these different types of protons and their corresponding ^{1}H NMR signals are indicated in the following figure-1.

The ^{1}H NMR spectrum of 2-Bromo-2-methyl-propionic acid but-2-ynyl diester (BPDE) was displayed in figure-2. In the ^{1}H NMR spectrum, two singlets appeared at 1.843 ppm and 4.72 ppm for -C(Br)$(CH_3)_2$ and -CH_2O-(C=O)- protons, respectively. In both signals, the presence of two additional weak peaks suggested the presence of the conformers of this product. All these different types of protons and their corresponding signals are indicated in the following figure-2.



Scheme-2
Preparation of functional initiators BPE and BPDE

Conclusion

The initiators of BPE and BPDE were synthesized by one step reaction which involved on esterification of 2-Bromo-2-methylpropionyl bromide with 2-Butyn-1,4-diol in a good yield. The structure of initiators was characterized by ^{1}H NMR analysis. α-halo esters are good initiator for ATRP because of their fast initiation property.Terminal alkyl group containing BPE and mid alkyne group containing BPDE could be used as initiator for ATRP to obtain end and mid alkyne functional polymers, respectively and the reactive polymers are suitable precursor for alkyne-azide click reaction.

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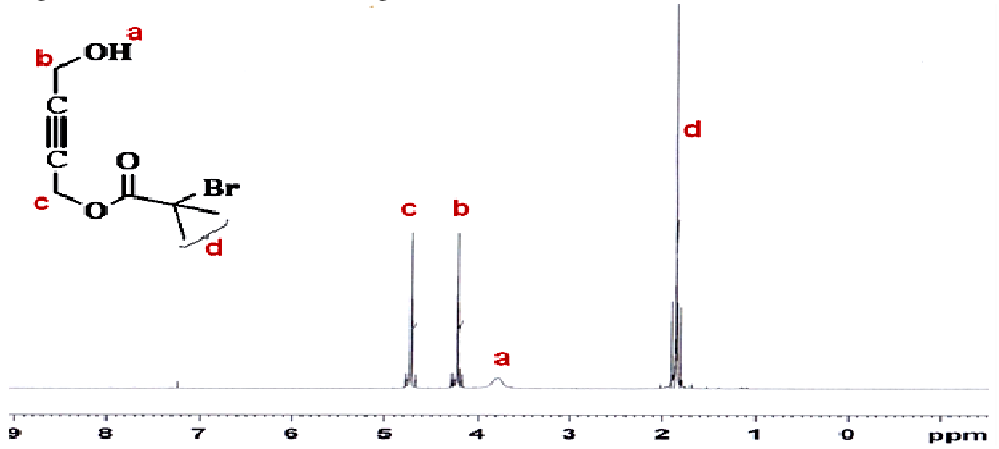

Figure-1
^{1}H NMR spectrum of initiator BPE

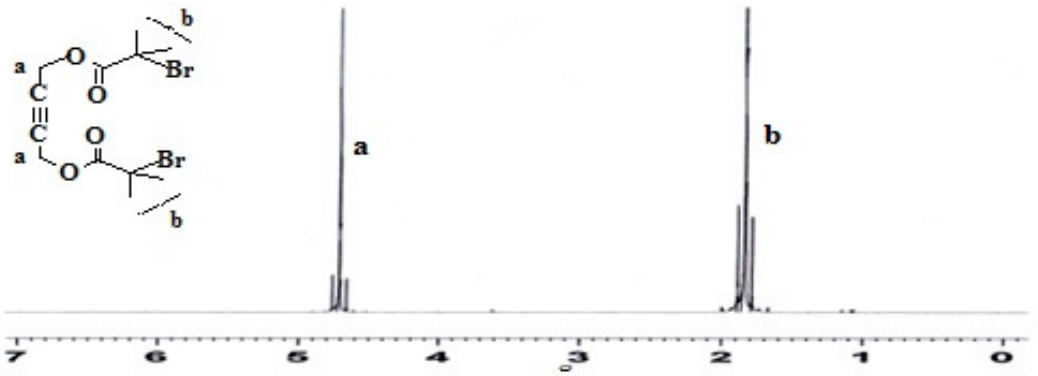

Figure-2
^{1}H NMR spectrum of BPDE

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