END GROUP FUNCTIONALIZATION OF REGIOREGULAR HEAD-TO-TAIL POLY(3-ALKYLTHIOPHENES)

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Introduction

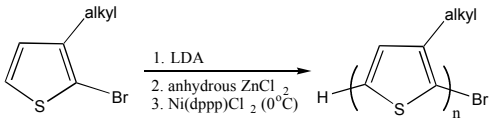
Conjugated polymers have received intense interest due to their practical and potential applications for electronic and photonic materials and devices. Poly-3-alkylthiophenes (PATs) represent a large portion of this field because of their good solubility, environmental stability and processability. Control over the regiochemistry and cross-coupling of 3-substituted thiophene monomers was achieved by using either organomagnesium[1] or organozinc[2] cross-coupling methods on active thiophene intermediates using Ni(II) catalysts. Such defect-free, structurally homogeneous, head-to-tail coupled polythiophenes (HT-PTs) have improved electronic and photonic properties over regiorandom analogues.[1]

Although poly(3-alkylthiophenes) can now be considered as well-studied and easily prepared polymers, less attention has been given to the nature of the polymer end groups.[3,4] Recently, we found that MALDI-TOF could successfully monitor the end group modification of PATs.[3,5] End group modification of these polymers would lead to the preparation of telechelic and/or functional PATs, which could extend the application of this class of conducting polymers. Because of this motivation, we put a great deal of effort in the end-group analysis and end-group modification of regioregular, head-to-tail poly(3-alkylthiophenes).

Results and Discussion

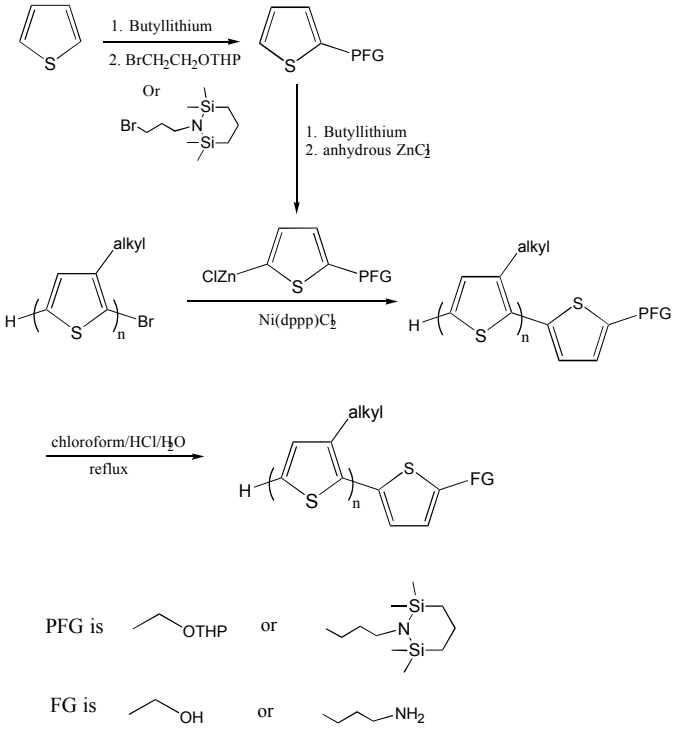
McCullough method and Rieke method are usually employed to prepare regioregular PATs.[1,2] Regioregularity of polymers obtained with these two routes can be as high as 99%. However, it is very difficult to obtain PATs with clean end group composition. MALDI MS has revealed the presence of three types of polymer chains: terminated with two hydrogen (H/H), one hydrogen and one bromine (H/Br), and two bromine (Br/Br) respectively.[3] The Br/Br comes from the homocoupling side reaction during the polymerizations. The originality of H/H is not clear. It may be from the side reaction such as metal-halogen exchange during the catalysis. The relative abundances of these three chains were largely a function of the polymerization conditions, such as the quantity of reagents employed, the monomer purity, the amount of catalyst added and polymerization time.

After careful investigation, we found it is possible to lower the portion of H/H and Br/Br (less than 10%) through controlling the polymerization conditions. Figure 1 shows the MALDI of a poly (3-hexylthiophene) sample. The polymer was prepared with a modified McCullough method (Scheme 1). It has a high percentage of H/Br end-groups (about 90% by peak area integral of MALDI MS). The polydispersity of this polymer is very low (PD = 1.18 by GPC and 1.10 by MALDI) because it has been extracted with hexane and CH_2Cl_2. The regioregularity of this well-defined polymer is about 99% head-to-tail by NMR.



Scheme 1. Synthesis of regioregular head-to-tail poly(3-alkylthiophenes) with modified McCullough method

Our strategy for end group functionalization is shown in Scheme 2. The well-defined PATs (narrow polydispersity, high regioregularity, pure end group composition) with bromine end groups reacted with organozinc compounds bearing protected functional groups such as hydroxyl, amino, etc. After deprotection , the well defined PATs with one functional end group was then obtained. The thienyl zinc chloride bearing protected functional groups were easily prepared by the reaction of thienyl lithium with 2-(2-bromoethoxy) tetrahydro-2*H*-pyran or 1-(3bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane. MALDI MS was intensively employed to monitor the end group transformation. After the poly(3-hexylthiophene) in Figure 1 reacted with 5-(2-ethoxy)tetrahydro-*2H*-pyran-2-thienyl zinc chloride, the polymer was end-capped with hydroxyl group protected by THP. The clean end group capping has been confirmed by the MALDI MS (Figure 2). After deprotection, the well defined poly(3-hexylthiophene) with hydroxyl end group was obtained (Figure 3). NMR also clearly confirmed the success of the end group fuctionalization.



Scheme 2. Synthetic procedure to make end group functionalized PATs.

Using the same approach, we also prepared well-defined PATs with functional end groups of amine. We are investigating the application of these end group functionalized PATs, such as preparation of diblock copolymers or self-assembled monolayer of PATs. We will report the results in due courses.

Experimental

Materials. 2-(2-bromoethoxy) tetrahydro-2*H*-pyran and 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane were purchased from Aldrich.

Instrumentation. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by Perseptive Biosystems. The information of sample preparation and instrumental conditions can be found in the reference.[3]

2-(2-thiopheneethoxy) tetrahydro-2H-pyran. 8.4g (0.1 mol) of thiophene was dissolved in 40ml of anhydrous THF. 40 ml of 2.5M Butyllithium solution was then inserted into the solution at -40^0C. After stirring at that temperature for half an hour, 20.9g of 2(2-bromoethoxy)tetrahydro-2H-pyran was added. The solution was then warmed up to room temperature and kept stirring at that temperature over night. After extraction with water/ether, the organic layer was dried with anhydrous sodium carbonate. After removing the solvent, the product was distilled out at75^0C (0.05mm).

1-(2-thiophenepropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane. The procedure is same as above. After the reaction of thienyl lithium with 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, the solution was extracted with water/ether. After removing of the solvent, the product was obtained without further purification. The purity was > 98% by GC-MS.

End Capping of regioregular head-to-tail PATs. Typically, to a 100ml flask, 20ml THF and 0.0025mol of 2-(2-bromoethoxy) tetrahydro-2*H*-pyran or 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-di-silacyclopentane

were charged. After cooling down to –40^{0}C, 5mmol LDA solution was inserted. The solution was kept stirring at that temperature for half hour, followed by the adding of 0.8 g of anhydrous $ZnCl_2$. The solution was then warmed up to room temperature slowly. This organozinc solution was transferred to a solution of 0.2g poly(3-hexylthiophene) (the average Mn is about 6K-8K by MALDI) in 80ml of THF. After the adding of 0.08g of Ni(dppp)Cl_2, the solution was kept stirring at 60^{0}C for 5 hours. The polymer was then precipited out in methanol and extracted with methanol. The yield was >95%.

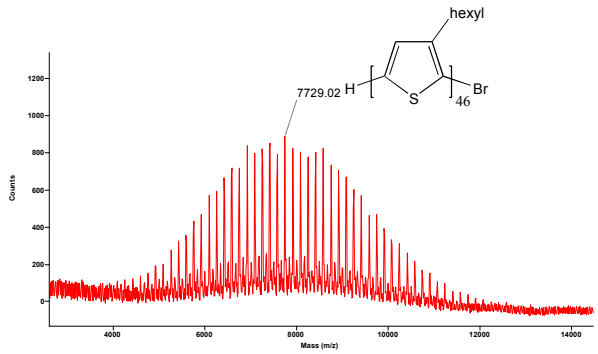


Figure 1. MALDI MS of well-defined poly(3-hexylthiophene) (average Mn = 7544, PD = 1.10 by MALDI; average Mn = 16,800, PD = 1.18 by GPC with polystyrene as standard)

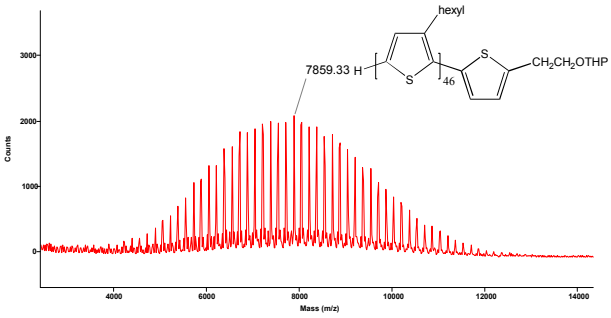


Figure 2. MALDI MS of well-defined poly(3-hexylthiophene) capped with (2-thiopheneethoxy)tetrahydro-2H-pyran (average Mn = 7664, PD = 1.08)

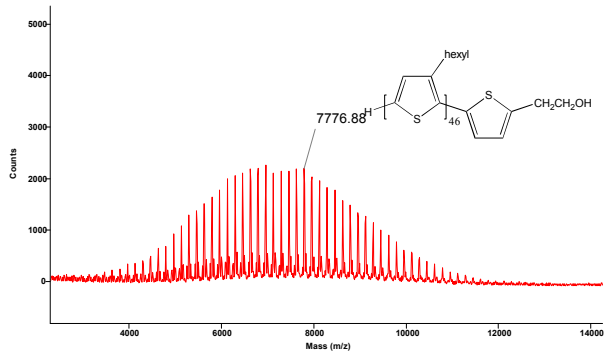


Figure 3. MALDI MS of well-defined poly(3-hexylthiophene) with hydroxyl end group (average Mn = 7510, PD = 1.13)

Conclusions

Well-defined poly(3-alkylthiophenes) could be prepared with modified McCullough method. End group functionalization (hydroxyl, amino) of these polymers have been achieved through the postpolymerization reaction with thienyl zinc chloride bearing protected hydroxyl or amino groups. The MALD MS could successfully monitor the end group modification clearly.

Acknowledgement. We are grateful to the NSF (CHE 9807707) for financial support.

References

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