Communications

Synthesis of Conjugated Polymer by the Stille Coupling Reaction

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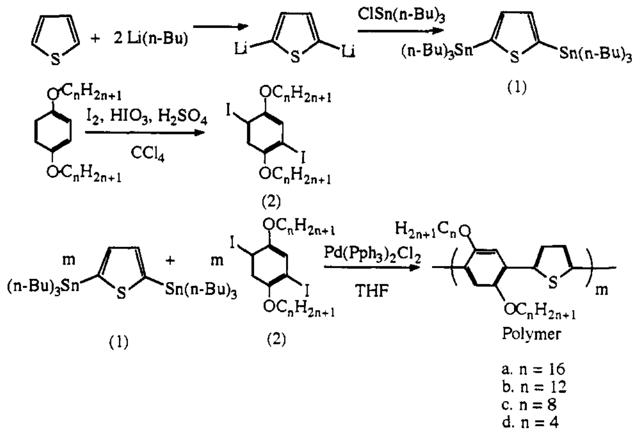
One of the current focuses for electroactive polymers is on the enhancement of electroactivity and processibility.[1] For example, the conductivity of polyacetylene has been dramatically increased by modifying the Shirakawa's catalyst.[2] Because the traditional conjugated polymers are usually insoluble, structural modifications of these polymers have been strongly pursued.[3] Two approaches have been developed to prepare processible polymers. The first approach involves a precursor preparation, such as Durham polyacetylene via ring-opening metathesis polymerization[4] and poly(phenylenevinylene) via bis-sulfonium salt polymerization,[5] all followed by a thermal elimination step. The second approach involves the synthesis of derivatized monomers such as 3- or 3,4-alkylated thiophene monomers followed by electrochemical or chemical polymerization.[3] The main disadvantage of the first approach is that it inevitably introduces defects into the final polymers which will reduce the electroactivity of the materials. The second approach has limitations in the choice of monomer which can be introduced and tolerated by the polymerization step.

Our research goal is to develop new polymerization methodology to prepare novel electroactive and nonlinear optically active materials. We find that the Stille reaction has the potential to be developed as a new polymerization tool.[6,7] This reaction mainly involves the coupling reactions of organic tin compounds with organic halides, triflates, carbonyl chlorides, etc. The reaction is catalyzed by palladium compounds and carbon–carbon single bonds are formed (see Scheme I). The reaction conditions are very mild and many functional groups can be tolerated in the reactants, such as amines, alcohols, esters, ethers, etc. The reaction yield is usually high. Clearly, if we properly choose monomers which are difunctionalized, we should be able to prepare conjugated polymers. This communication reports an example demonstrating the feasibility of the Stille reaction in preparing processible conjugated polymers.

The synthesis of monomers and polymers are shown in Scheme I. Compound 1 was synthesized by the reaction of dilithiothiophene[8] with tributyltin chloride. Compounds 2 with different length of alkyl chain (n = 16, 12, 8, 4) were synthesized according to the literature procedure.[9,10] The polymerization was easily carried out in THF in the presence of a catalytic amount (5% mol) of $Pd(PPh)_2Cl_2$ under a nitrogen atmosphere. The reaction went smoothly and the polymer was precipitated into acetone by which the tin compound was removed. The polymers a, b, and c are soluble in different organic solvents, such as THF, chloroform, and dichloroethane etc. Uniform, optical-quality films can be cast on glass slides and can be peeled off by simply dipping them into water. The polymer d has a limited solubility in THF and precipitated out during polymerization.

Scheme I.



The direct support for the polymerization outlined in the Scheme I comes from the polymer analysis. For example, GPC measurements of polymer a, using a Waters RI system, indicated a number-average molecular weight of ca. 14 000 g/mol against the polystyrene standards, which corresponds to about 22 repeat units. Elemental analysis indicated a close match with the theoretical values (For example, for polymer a, predicted C, 78.94, H, 11.04; found C, 76.97, H, 11.46%). This polymer was stable up to 400 °C under a nitrogen atmosphere, as shown in the TGA studies. Due to the existence of the long alkyl chains, the T_g value of this polymer was low, at about 45 °C, and a melting process started at about 61 °C as indicated by the DSC studies. These results demonstrate that this polymer is both soluble and fusible, allowing easy processing. A reversible thermochromism was noted in this polymer; when it was heated, the color of the polymer changed from red to yellow, returning to red when it was cooled down to room temperature. This phenomenon might be associated with the polymer's structural transition from rigid-rod to coil main chain, as observed in the

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[10] All of the monomers gave rise to satisfactory NMR and mass spectra. Compound 1: ^{1}H NMR δ ($CDCl_3$), *n*-butyl proton at 0.85 (t), 1.20 (m, multiplet), 1.35 (m), 1.6 (m), thiophenyl proton at 7.35 ppm (s). M_{max}^+ 661. Compound 2: ^{1}H NMR δ ($CDCl_3$), alkyl proton at 0.85 (t), 1.30 (broad singlet), 1.50 (m), 1.75 (m), 3.90 (t), phenyl proton at 7.15 (s) ppm. M_{max}^+ 810.

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poly(3-alkylthiophene).[11]

The ^1H NMR spectrum of the polymer a is dominated by the chemical shift of the side alkyl chain at 0.90 ($-CH_3$), 1.20–1.40 ($-(CH_2)_{12}-$), 1.50 ($-O-C-C-CH_2-$), 1.95 ($-O-C-CH_2-$), 4.20 ($-O-CH2-$). The chemical shifts of the thiophenyl proton and the phenyl proton appear at 7.3 and 7.5 ppm, respectively. The FTIR spectrum shows a strong absorption due to the ether linkage at 1216 cm^{-1}; the C–H stretching of $-CH_2$ and $-CH_3$ appear at 2851 and 2920 cm^{-1}, and the out-of-plane mode of the $-C-H$ bonds of the phenyl and thiophenyl rings appear at 857 and 804 cm^{-1}. The absorptions due to $>C{=}C<$ stretching of the benzene and thiophene ring are medium, at 1604 and 1556 cm^{-1}, respectively. All other polymers showed similar spectroscopic features.

These polymers represent a very interesting class of polymers, a benzene and thiophene alternating copolymer. Poly(*p*-phenylene) has a bandgap of 3.0 eV (413 nm), and the bandgap of polythiophene is 2.1 eV (590 nm).[12] This polymer, however, has a bandgap which falls in between those of the poly(*p*-phenylene) and the polythiophene, ca. 2.38 eV (520 nm; see Figure 1). It was also found that these polymers exhibited a strong fluorescence when exposed to the visible light. The emission spectrum of the polymer a solution in THF showed a peak at 525 nm which coincides with the band gap, indicating that it is a localized excitation. However, a shoulder at 565 nm can also be noted in the emission spectrum (see Figure 1). This might be due to structural relaxations, such as the formation of polaronic and bipolaronic species.[13,14] The luminescent property of these polymers offers an opportunity to study electroluminescence. Quantitative studies involving the fabrication of the electroluminescent diode and the measurements of the quantum yield in the polymer thin film are in progress. This polymer is also found to be nonlinear optically active, a $\chi^{(3)}$ value of 1.77×10^{-13} esu for polymer a was determined in a solution with a concentration of 0.527 g/L in chloroform by using degenerate four wave mixing (the pure chloroform has a $\chi^{(3)}$ value of 0.602×10^{-13} esu at 532 nm).

There are only two known attempts to make this kind of polymer. One approach was by the thiophenation of a poly(phenylene-α,ω-diketone) precursor polymer using Lawesson's reagent.[15] The resulting material was a black, insoluble material. The second approach utilized the Grignard reagents from a thiophene dibromide, resulting in a similar polymer.[16] However, the Grignard reagent is very sensitive to moisture and is very reactive toward different functional groups such as esters, amines, and alcohols. Therefore, the reaction scope is limited. In contrast, the Stille reaction offers much more flexibility in the selection of both the monomers and the reaction conditions; we are exploring the potentials of this reaction in polymerization.

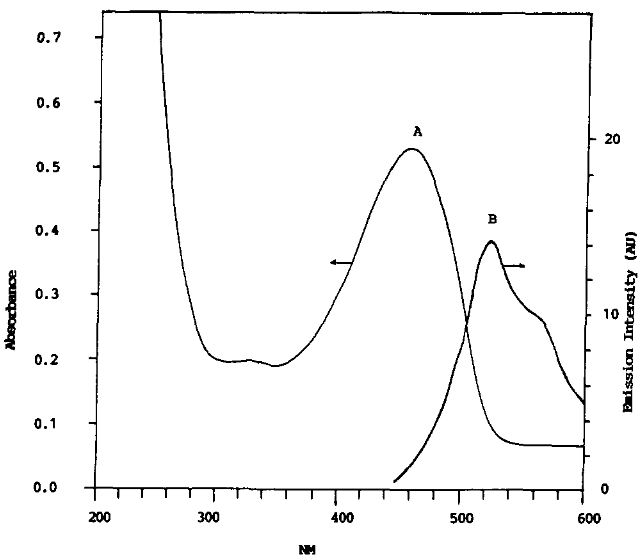

Figure 1. UV–vis spectrum (curve A) and fluorescence spectrum (curve B) of the polymer, the arrows refer to the ordinates of corresponding spectrum. All of the spectra were measured in THF. The concentration for the absorption spectrum is 0.0012 g/100 mL and for the emission spectrum is 0.000 24 g/100 mL.

In summary, the coupling reaction between organic halide and organic tin compounds was utilized to synthesize soluble and fusible conjugated polymers. The rich access in monomers, the mild reaction condition and the tolerance to different substituents make this reaction versatile in synthesizing new conjugated polymers.

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