JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Water- and Ionic-Liquid-Soluble Branched Polythiophenes Bearing Anionic and Cationic Moieties

Thomas V. Richter,[§,#,‡,⊥] Christian Bühler,[§,⊥] and Sabine Ludwigs[§,#,‡,*]

[‡]Institut für Polymerchemie, Universität Stuttgart, 70569 Stuttgart, Germany

[#]School of Soft Matter Research, Freiburg Institute for Advanced Studies, Universität Freiburg, 79104 Freiburg, Germany

[§]Institut für Makromolekulare Chemie and Freiburger Materialforschungszentrum, Universität Freiburg, 79104 Freiburg, Germany

Supporting Information

ABSTRACT: The synthesis of ionically functionalized branched polythiophenes with either carboxylic acid (anionic, **P3T-COOH**) or methylimidazolium (cationic, **P3T-MIM**) end groups is presented. Due to the large number of end groups present in the polymer, the functionalization has a major impact on the solubility of the polymers. In the case of **P3T-COOH**, the polymer shows a fully reversible phase transfer between organic solvents and water, depending on the pH. Remarkably, the ionic-liquid-modified polymer **P3T-MIM** is soluble in a room-temperature ionic liquid. The absorption properties are unaffected by the functional end groups.

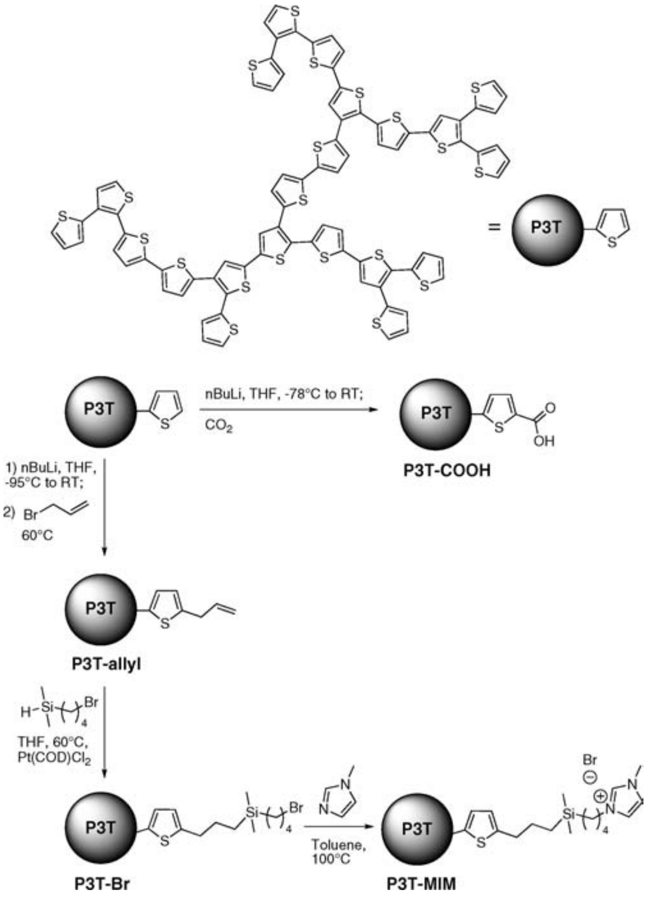
Conjugated polymers are highly interesting materials that find applications in solution-processed electronic devices such as electrochromic windows,[1] organic solar cells,[2] field effect transistors,[3,4] and light-emitting diodes.[5] The properties of the materials can be influenced by either the development of completely new building blocks, which typically requires large synthetic efforts, or the functionalization of established polymers. A postpolymerization functionalization (polymer analogous reaction) to influence the materials' properties is appealing and versatile since established polymers can be modified and used as platforms for new polymers with tailor-made properties. Functionalization of conjugated polymers with anionic or cationic charged side groups[6] leads to a group of polymers known as conjugated polyelectrolytes (CPEs). The charged groups, e.g., sulfonate,[7,8] carboxylate,[9] or imidazolium,[10] covalently attached to the backbone can render the polymer soluble, for example, in water. Water-soluble conjugated polymers are attractive, as they can be processed by more environmentally friendly methods and also be used in biological environments. Additionally, the ionic groups allow the polymer to interact with chemical substances, ions, or DNA, which could lead to applications such as bio- and chemosensors.[10−12] Recently, branched conjugated oligomers and polymers evoked interest due to their good solubility in organic solvents and their isotropic optoelectronic properties in contrast to linear conjugated polymers such as poly(3-hexylthiophene).[13] Advincula[14] and Bäuerle,[15] for example, reported the synthesis of thiophene-based dendrimers. Phosphonic acid-functionalized oligothiophene dendrimers were used for the stabilization of CdSe nanoparticles,[16] and cyanoacrylic acid-functionalized oligothiophene dendrimers with arylamines in the periphery were used as metal-free dyes in dye-sensitized solar cells.[17] We recently reported the synthesis of hyperbranched polythiophenes in a one-pot reaction based on oxidation polymerization with $FeCl_3$.[18] The materials showed hole-conducting properties and were tested in organic solar cells.[19] Concerning the functionalization, branched conjugated architectures have a high density of end groups compared to their linear analogues. Very recently, the group of Bunz reported on the synthesis of hyperbranched poly(phenylene vinylene−phenylene ethynylene) polymers bearing iodine groups.[20,21] The authors highlighted the easy postfunctionalization of the hyperbranched polymers with a variety of functional groups, e.g., amines, phosphines, phenol derivatives, carboxylic esters, or fluorinated groups, due to the high concentration of end groups. In the case of a carboxylic ester-functionalized hyperbranched poly(phenylene vinylene−phenylene ethynylene), the authors obtained polymers that were soluble in water/methanol mixtures after hydrolysis.[21]

In this Communication we present the synthesis of anionically and cationically functionalized branched polythiophenes using a postpolymerization approach based on the facile deprotonation of thiophene end groups with butyllithium. The synthetic routes are shown in Scheme 1. **P3T** was used as the parent branched polythiophene and was synthesized as shown earlier.[18] The molecular weight (Mw) and the polydispersity index (PDI) were determined to be 1650 g/mol and 1.74 by size exclusion chromatography against polystyrene standards. The key step in the postpolymerization functionalization is the deprotonation of **P3T** with butyllithium to create nucleophilic centers that can subsequently be reacted with different electrophiles.

The synthesis of the carboxylic acid-functionalized branched polythiophene was conducted in a one-step procedure by the deprotonation of **P3T** and the subsequent reaction with CO_2 (a detailed description is given in the Supporting Information (SI)). **P3T-COOH** was obtained after acidic workup of the reaction mixture. The IR spectrum of **P3T-COOH** (Figure 1A) shows a strong band at 1690 cm^{-1} which is not present in the spectrum of **P3T** and can be ascribed to the carboxylic acid groups present in the polymer. The other bands marked in the spectrum are also found in thiophene-2-carboxylic acid, which can be used as a model compound.[22] A polyanion with

Received: August 15, 2011
Published: December 14, 2011

Scheme 1. Functionalization of Branched Polythiophene P3T with Carboxylic Acid (P3T-COOH) and Methylimidazolium End Groups (P3T-MIM)



carboxylate anions in the periphery can be formed from **P3T-COOH** upon deprotonation by a base. In a layer-by-layer (LbL) assembly[23] with polyethylenimine (PEI, Lupasol WF by BASF) as model system, well-defined layers could be obtained by the *in situ* deprotonation of **P3T-COOH** by the polyamine. A precleaned glass substrate was first dipped in a PEI solution in THF (0.1 mg/mL). The substrate was then washed twice in pure THF to remove any PEI not adsorbed on the surface. The substrate was next dipped in a solution of **P3T-COOH** in THF (0.1 mg/mL). After rinsing twice in pure THF, the first double layer was obtained. This process was repeated nine times. After each double layer, an absorption spectrum was recorded to follow the deposition. The optical density (OD) at a certain wavelength of the sample can be taken as a very convenient indicator for monitoring the film thickness. The linear correlation in Figure 1B suggests a linear growth of the thickness of the polymer multilayer film with the number of deposited double layers. In other words, each double layer has the same thickness within error, indicating a very defined process. Combination of **P3T-COOH** with a cationically modified conjugated polymer should further allow combination of materials in thin films with potential applications, for example, in bulk heterojunction solar cells.[24]

In the case of the cationic functionalization (Scheme 1), all reaction steps were tested for their feasibility by model reactions with a branched terthiophene as low-molecular-weight model compound, and the reactions were then transferred to the polymeric system (see SI). In the first step, the deprotonated **P3T** was reacted with 3-bromopropene to obtain an allyl-functionalized, branched polythiophene (**P3T-allyl**). The degree of functionalization was determined using NMR spectroscopy and MALDI-TOF mass spectrometry. In both cases, a degree of functionalization of about 65% was found. In Figure 2A, a MALDI-TOF detail spectrum of **P3T-allyl** is shown for a degree of polymerization of 4 (full spectrum in the SI). The subdistribution is caused by the presence of different numbers of allyl end-groups, with a maximum of four allyl groups per polymer molecule. The small peaks presumably represent oxidized polymer species, which can stem from either the oxidation of the polymer in air or the acidic matrix used for the MALDI-TOF measurements. As the amount of oxidized species varied for different measurements and the branched polythiophene has a rather low-lying HOMO level,[18] the oxidation in the MALDI-TOF matrix seems to be more likely. As can be seen in Figure 2A, the MALDI-TOF spectrum also shows peaks that can be assigned to seven-fold substitution of the polymer. As only six α-H positions are present in the parent polymer molecule with a degree of polymerization of 4, this suggests that also β-functionalization can occur (for further MALDI-TOF spectra see SI). To obtain a bromoalkyl-functionalized, branched polythiophene (**P3T-Br**), the terminal double bonds of **P3T-allyl** were further reacted with (4-bromobutyl)dimethylsilane in a hydrosilylation reaction with Pt(COD)Cl$_2$ as catalyst. Examination of the product by NMR spectroscopy revealed a conversion of double bonds of ~85%, resulting in an overall degree of functionalization with bromoalkyl end groups of 55%. In the last step, **P3T-Br** was reacted with *N*-methylimidazole in a nucleophilic substitution reaction to obtain a polycationic methylimidazolium-functionalized, branched polythiophene (**P3T-MIM**). The substitution of bromine end groups by methylimidazole was quantitative, as

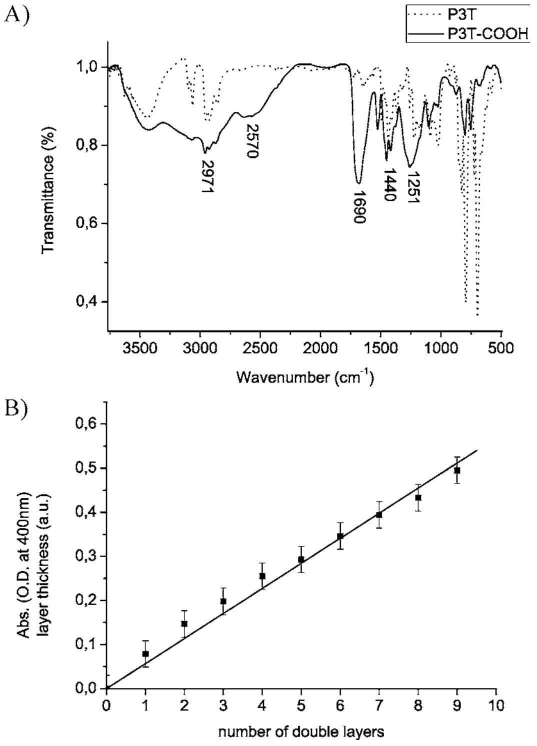


Figure 1. (A) IR spectra of **P3T** and **P3T-COOH**. (B) Absorption of LbL-assembled **P3T-COOH**:PEI multilayers depending on the number of deposited double layers.

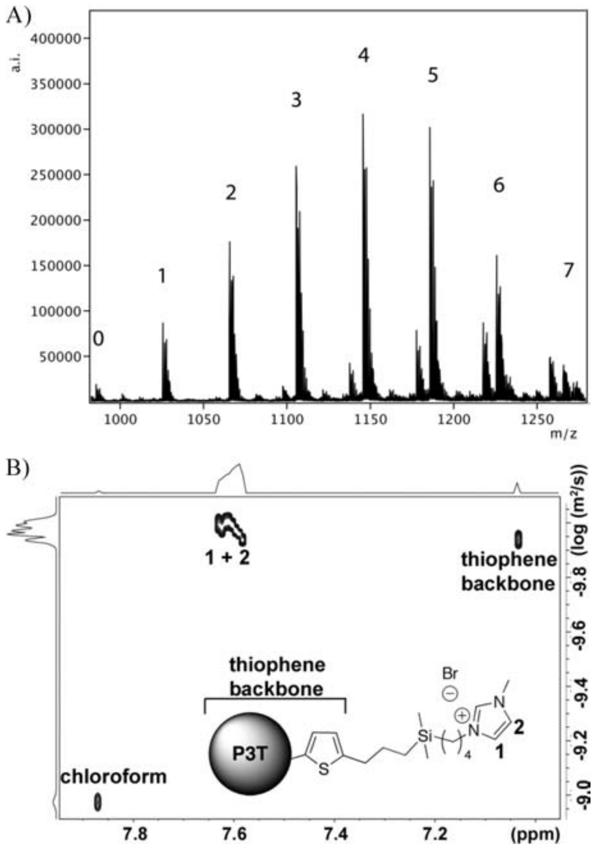


Figure 2. (A) MALDI-TOF detail spectrum of **P3T-allyl** for a degree of polymerization of 4; the number of allyl groups present in the polymer molecules is indicated. (B) Contour plot DOSY ^{1}H NMR spectrum of **P3T-MIM** in $CDCl_3$/DMSO-d_6 (1:1 v/v). The spectrum is referenced to DMSO-d_6.

shown by ^{1}H NMR measurements. We find an overall functionalization of the polymer with imidazolium end groups of 55%. NMR spectra of the functionalized polymers together with the spectra of the respective low-molecular-weight model compounds are provided in the SI. To rule out the presence of free methylimidazole in the polymer **P3T-MIM**, diffusion-ordered spectroscopy (DOSY) ^{1}H NMR measurements were conducted in a $CDCl_3$/DMSO-d_6 mixture (1:1 v/v), Figure 2B. The shown region between 7 and 8 ppm contains characteristic peaks of the polythiophene core as well as of the methylimidazolium moieties and the chloroform signal. The peaks corresponding to the polythiophene core and the methylimidazolium moiety have the same diffusion coefficient, indicating that the methylimidazolium groups are bound to the polymer backbone. This is further supported by the diffusion coefficient found for chloroform, which significantly differs from the polymer signals due to the much smaller size. In terms of solubility in organic solvents, **P3T-MIM** is not soluble in chloroform (a good solvent for **P3T**) but well soluble in chloroform/acetonitrile mixtures.

One feature which can be strongly influenced by the ionic end groups is the solubility in so-called green solvents including water and ionic liquids.[8,9] The functionalized branched polythiophenes **P3T-COOH** and **P3T-MIM** were found to show very distinct solubilities as compared to their parent polymer **P3T**. Carboxylic acids have the advantage of being switchable in polarity by the degree of deprotonation; i.e., they are pH-sensitive. We used this effect to tune the solubility of **P3T-COOH** between organic solvents and water. For this, **P3T-COOH** was dissolved in a mixture of THF and $CHCl_3$ (1:1 v/v). To these solutions was added water to form an aqueous phase on top of the organic phase. One drop of either a NaOH solution (1 M) or a HCl solution (1 M) was then added. In Figure 3A (left), the two vials are shown. Depending on the pH, either the lower organic phase or the upper aqueous phase is colored. This phase transfer of **P3T-COOH** is fully reversible and can be repeated several times upon changing the pH. The neutral, protonated polymer is better soluble in the organic phase, whereas the deprotonated polyanion dissolves better in the aqueous phase. Solubility of materials in ionic liquids has become an active area of research, because these solvents offer the advantage of high electrochemical stability, very low vapor pressures, and high thermal stabilities.[25] A number of publications deal with electrodeposition or electropolymerization in ionic liquids as electrolyte (reaction medium).[26−29] Interestingly, we found that the conjugated polyelectrolyte **P3T-MIM** is well soluble in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate (Figure 3A, right vial). This is one of the few reported examples of a conjugated polyelectrolyte that is soluble in ionic liquids.[30] Applications in sensors or electrochemical devices are two promising routes. It was, for example, shown that π-conjugated polymers being electrochemically cycled in ionic liquids can have very long lifetimes.[31] To test if the optical absorption properties of the conjugated polythiophenes are altered due to the ionic end groups, optical absorption measurements were carried out in solution. In Figure 3B, the UV−vis absorption spectra of the different polymers are displayed. One can see that the onsets and maxima of **P3T-MIM** are only slightly altered with respect to the parent polymer **P3T**. This implies that the functionalization does not affect the π-conjugated system of the polymer. Also the use of different solvents (chloroform/acetonitrile mixture or ionic liquid) does not seem to have an influence on the

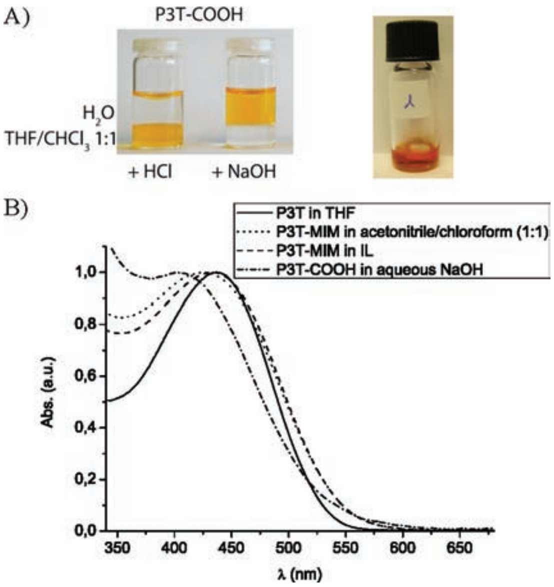


Figure 3. (A) Solubility of **P3T-COOH** depending on the pH (left) and solubility of **P3T-MIM** in the ionic liquid (IL) 1-ethyl-3-methylimidazolium diethylphosphate (right). (B) Absorption spectra of **P3T**, **P3T-MIM**, and **P3T-COOH** in different solvents.

absorption properties. For **P3T-COOH** in aqueous NaOH, the absorption maximum is slightly blue-shifted with respect to **P3T**. A blue shift of the absorption spectrum of polythiophenes upon carboxylic acid functionalization was also observed by Lohwasser et al.[32] In **P3T-MIM**, the cationic species are separated from the polymer π-system by spacers.

In conclusion, we have shown that branched conjugated polythiophenes can be used as starting materials for new conjugated polyelectrolyte materials with tunable solution properties. Anionic and cationic branched polythiophenes were presented. Carboxylic acid functionalization of the branched polythiophene was achieved by a simple deprotonation of terminal thiophene units and the subsequent reaction with CO_2. A fully reversible and complete phase transfer between an aqueous and an organic phase could be achieved upon changing the pH. Furthermore, it was shown that the polymer can be processed into defined multilayers by a simple layer-by-layer deposition technique. Cationic functionalized branched polythiophenes in which the methylimidazolium cation is separated from the π-conjugated system of the polymer by an alkyl spacer were synthesized via a versatile synthetic route. Our route allows on the one hand the variation of the alkyl spacer length, on the other hand a number of different end groups is accessible by the use of different nucleophiles. Alkylimidazolium cations are well known in the area of ionic liquids, and we could show the solubility of an imidazolium-functionalized conjugated polymer in an ionic liquid. Conjugated polyelectrolytes as presented in this work can combine characteristics of both material classes, conjugated polymers and polyelectrolytes, i.e., electronic and ionic conduction. This may lead to very interesting new materials with possible applications in sensing, dye-sensitized solar cells, or electrochromic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, NMR, and DSC. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

sabine.ludwigs@ipoc.uni-stuttgart.de

Author Contributions

[⊥]These authors contributed equally to this work.

■ ACKNOWLEDGMENTS

The authors thank Prof. Dr. R. Mülhaupt for stimulating discussions, Dr. R. Hanselmann, M. Waitl, and A. Hasenhindl for MALDI-TOF and NMR measurements, S. Link & H. Mangold for CV measurements, and BASF SE for the donation of the Lupasol WF. The DFG is acknowledged for financial support within the framework of the priority program SPP-1355 and the Emmy-Noether program. This work was further supported within FRIAS by the Excellence Initiative of the German Federal and State Governments.

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