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Grafted conjugated polymers: synthesis and characterization of a polyester side chain substituted poly(*para*phenyleneethynylene)†

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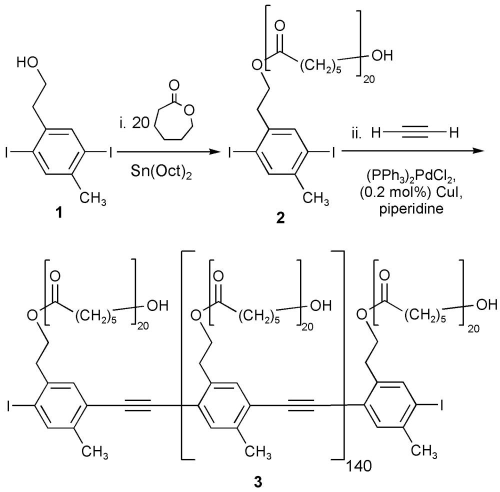
The synthesis of a poly(*para*phenyleneethynylene) with macromolecular side chains and its irreversible thermochromic behaviour are reported herein.

Poly(*para*phenyleneethynylene)s (PPEs)[1] are a specific class of conjugated polymers in which benzene groups are linked by alkyne units. Their high fluorescence quantum yield and their well developed chromicity[2,3] make the PPEs attractive as sensors[4] and as active layers in semiconductor devices.[5,6] While structural variations on PPEs[7–11] have been reported, to our knowledge, PPEs with macromolecular substituents have not been described. Such graft copolymers would be of interest a) as novel macromolecular architectures, b) as a means to obtain the optical properties of PPEs in the solid state at high intrinsic backbone dilution, and c) as embedded, nanoscale separated materials with potentially unusual mechanical and solubility properties.

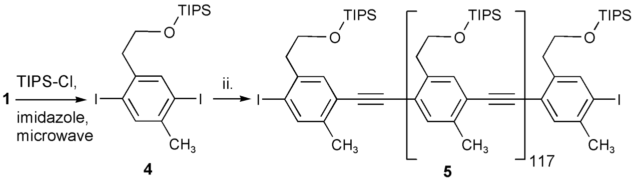
The synthesis of a grafted PPE starts by reacting **1** with ε-caprolactone catalysed by Sn(O–C=OCHEtBu)$_2$. The telechelic macromonomer **2** (Scheme 1) forms in 48% yield. It is dissolved in a mixture of THF and piperidine. Addition of a trace of $(Ph_3P)_2PdCl_2$ (0.2 mol%), CuI, and a measured quantity of acetylene gas[12] furnishes a deep-yellow, flaky material after precipitation from methanol. The color and the following gel permeation chromatography (gpc, *vs.* polystyrene) showed that **3** had formed in 78% yield. The gpc trace of **3** is monomodal but with a broad distribution of molecular weights. The polydispersity index (PDI) is 5.3 and the M_n of **3** is recorded to 336 × 10^3. The polymer has a degree of polymerization (P_n) of 140 repeating units. In the ^{13}C NMR spectra of **3** the resonances of the grafted-on polyesters are prominent, but the signals attributable to the conjugated main chain are weak and thus difficult to discern. Due to the substitution pattern at the benzene ring and the innate non-regioselectivity of the Pd-coupling, the alkyne carbons in **3** should show four resonances and the benzene rings should show six resonances in its ^{13}C NMR spectrum, exacerbating the problem of the low signal to noise ratio of the backbone carbon resonances. To demonstrate that Pd-catalysis works well for this substitution pattern (Scheme 2) we prepared a model polymer that shares the backbone with **3** but features simpler solubilizing groups.

The microwave-mediated coupling (5 min reaction time) of **1** with chlorotriisopropylsilane in imidazole furnished the monomer **4** in a 98% yield after chromatography as a colorless oil. Treatment of **4** under conditions optimized for the synthesis of **3** gave a high molecular weight polymer **5** that is soluble in halogenated organic solvents. At concentrations higher than 2.5 wt% **5** forms a blue-fluorescent *but clear* jelly in dichloromethane or in chloroform.

The aromatic and alkyne regions of the ^{13}C NMR spectrum of **5** are superimposable with that of **3** and shown in Fig. 1. As expected, the signals of the alkyne carbons and the benzene rings are split due to the non-equivalency of the side chains in the monomer **4** and the inset shows the split of the alkyne resonances at 92 ppm into four signals.



Scheme 1 Synthesis of the PPE **3** with a macromolecular polyester substituent. Yield of **2**: 48%, PDI = 1.3, M_n = 2.4 × 10^3 (gpc *vs.* polystyrene); yield of **3**: 78%, PDI = 5.3, M_n = 336 × 10^3 (gpc), P_n = 140.



Scheme 2 Synthesis of a PPE **5** with TIPS substituents. i. Yield of **4** = 98%. ii. See Scheme 1. Yield of **5** = 98%, M_n = 37 × 10^3 (gpc), PDI = 3.9, P_n = 117.

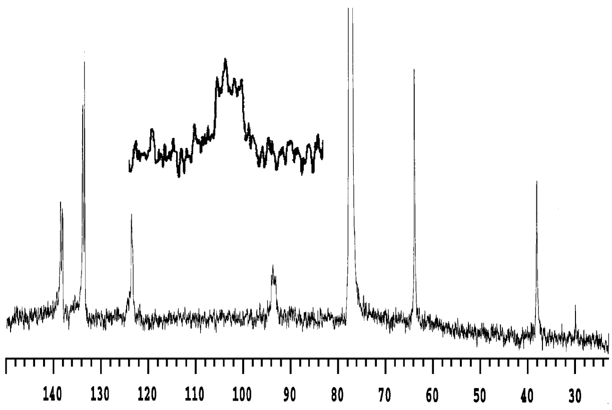


Fig. 1 ^{13}C NMR of model polymer **5**. Visible are the four alkyne peaks at δ = 92 (see inset) and the five resolved signals for the benzene rings. The large signal at δ = 77 is due to CDCl$_3$. TIPS signals are not shown. The signal at δ = 31 is a hydrocarbon impurity.

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† Electronic supplementary information (ESI) available: experimental, including details of preparation and spectroscopic characterization of all new compounds. See http://www.rsc.org/suppdata/cc/b3/b303699p/

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The UV-vis and emission spectra of the polymers **3** and **5** in chloroform solution and in thin films are shown in Fig. 2. Their optical properties are similar to each other and in accord with the spectroscopic data recorded for dialkyl-PPEs[1] where $\lambda_{\text{max (solution)}}$ is 388 nm and $\lambda_{\text{max (thin film)}}$ is 439 nm. The silyloxy substituent in **5** seems to have a slight electron withdrawing effect. As a consequence, λ_{max} (absorption) is somewhat blue-shifted in **5**. The optical properties of **3** in the solid state are unusual. As-spun films show a λ_{max} (absorption) of 436 nm, typical of dialkyl-PPEs. Upon annealing (4 h, 100 °C) these thin films, *their absorption changes back to* $\lambda_{max} = 406$ *nm, which is similar to the absorption of* ***3*** *recorded in chloroform* (Fig. 2). In addition, the absorption loses almost all structure. The emission of the films changes much less upon annealing and only a small shift from 519 to 504 nm is observed when going from the pristine to the annealed films. The fluorescence intensity does not change visibly upon annealing. At the same time the annealed thin films of **3** are now insoluble in common organic solvents.

We assume that the insolubility of the polymers upon annealing is due to an increased order in the polyester side chain. Powder X-ray diffraction (Fig. 3) shows that the intensity of the polyester diffraction peaks at 5.6, 4.14, 3.74, and 3.0 Å increases upon annealing, while a diffuse intensity of diffraction that is visible as a hump at 2-θ = 20–22° disappears during the annealing process. This broad diffraction peak at 2-θ = 20–22° is typical for the π–π-stacking of the PPEs and is the most intense diffraction in these materials.[13,14] The annealing increases the ordering of the polyester side chains, but it seems to *decrease* the ordering of the PPE main chain, *i.e.* in the competition of main chain and side chains, the side chains win and lead to a twist and a gross disorder of the PPE main chain in the solid. In the powder diffraction of the annealed sample there are no signs of the diffraction of the main chain left.

In conclusion we have made two new *dialkyl*-PPE derivatives **3** and **5** with a macromolecular polyester substituent and triisopropylsilyloxy side groups. The attachment of the polyester side chain to the PPE leads to a graft copolymer that shows an unusual chromic behavior, in that its λ_{max} (UV-vis) blue-shifts upon annealing. In future we will investigate the structural pecularities of both **3** and **5** further.

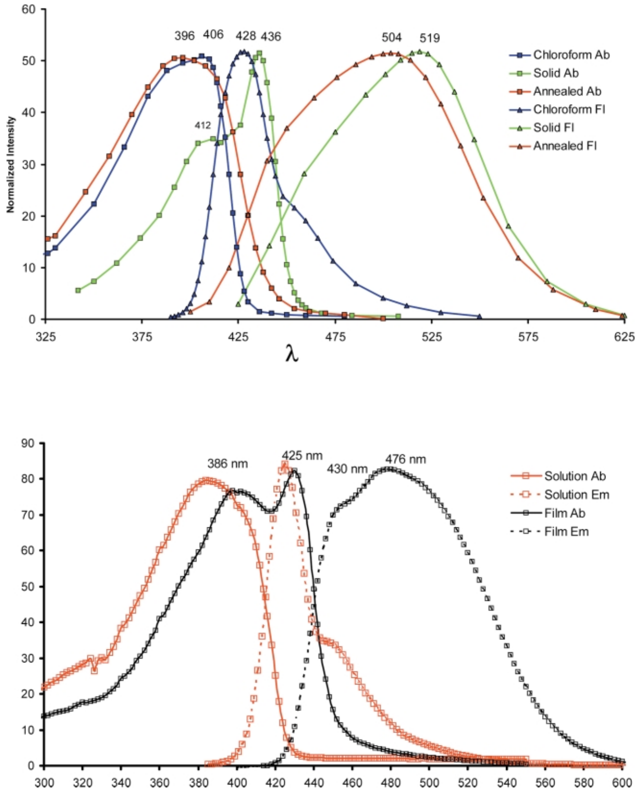

Fig. 2 UV-vis and emission spectra of **3** and **5**. Top: spectra of **3**; bottom: spectra of **5**.

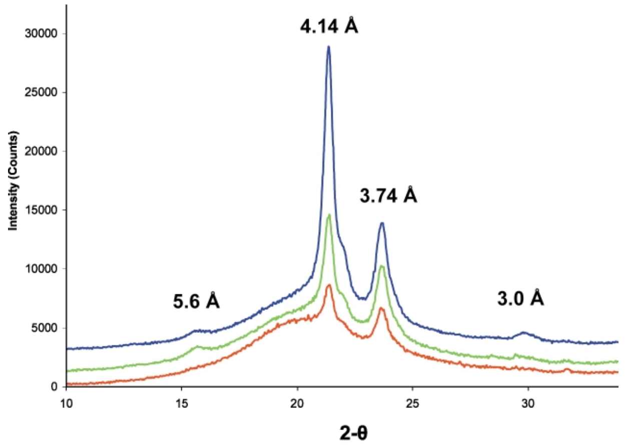

Fig. 3 X-Ray diffraction of different polyester substituted PPEs. Bottom curve: gel phase. Middle curve: pristine powder. Top curve: annealed powder.

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Notes and references

1 U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605; U. H. F. Bunz, *Acc. Chem. Res.*, 2001, **34**, 998.
2 C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer Martinez and U. H. F. Bunz, *Macromolecules*, 1998, **31**, 8655; T. Miteva, L. Palmer, L. Kloppenburg, D. Neher and U. H. F. Bunz, *Macromolecules*, 2000, **33**, 652.
3 J. Kim and T. M. Swager, *Nature*, 2001, **411**, 1030.
4 Q. Zhou and T. M. Swager, *J. Am. Chem. Soc.*, 1995, **117**, 12593; J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864; T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
5 A. Montali, P. Smith and C. Weder, *Synth. Met.*, 1998, **97**, 123; C. Schmitz, P. Posch, M. Thelakkat, H. W. Schmidt, A. Montali, K. Feldman, P. Smith and C. Weder, *Adv. Funct. Mater.*, 2001, **11**, 41; A. Kokil, I. Shiyanovskaya, K. D. Singer and C. Weder, *J. Am. Chem. Soc.*, 2002, **124**, 9978; C. Weder, C. Sarwa, A. Montali, G. Bastiaansen and P. Smith, *Science*, 1998, **279**, 835.
6 N. G. Pschirer, T. Miteva, U. Evans, R. S. Roberts, A. R. Marshall, D. Neher, M. L. Myrick and U. H. F. Bunz, *Chem. Mater.*, 2001, **13**, 2691.
7 T. Sato, D. L. Jiang and T. Aida, *J. Am. Chem. Soc.*, 1999, **121**, 10658.
8 J. N. Wilson, W. Steffen, T. G. McKenzie, G. Lieser, M. Oda, D. Neher and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2002, **124**, 6830.
9 S. Zahn and T. M. Swager, *Angew. Chem., Int. Ed.*, 2002, **41**, 4225.
10 C. Y. Tan, M. R. Pinto and K. S. Schanze, *Chem. Commun.*, 2002, 446; N. DiCesare, M. R. Pinto, K. S. Schanze and J. R. Lakowicz, *Langmuir*, 2002, **18**, 7785.
11 C. G. Bangcuyo, J. M. Ellsworth, U. Evans, M. L. Myrick and U. H. F. Bunz, *Macromolecules*, 2003, **36**, 546; B. Erdogan, J. N. Wilson and U. H. F. Bunz, *Macromolecules*, 2002, **35**, 7863; C. G. Bangcuyo, U. Evans, M. L. Myrick and U. H. F. Bunz, *Macromolecules*, 2001, **34**, 7592.
12 J. N. Wilson, S. M. Waybright, K. McAlpine and U. H. F. Bunz, *Macromolecules*, 2002, **35**, 3799.
13 U. H. F. Bunz, V. Enkelmann, L. Kloppenburg, D. Jones, K. D. Shimizu, J. B. Claridge, H.-C. zur Loye and G. Lieser, *Chem. Mater.*, 1999, **11**, 1416; L. Kloppenburg, D. Jones, J. B. Claridge, H.-C. zur Loye and U. H. F. Bunz, *Macromolecules*, 1999, **32**, 4460.
14 D. Ofer, T. M. Swager and M. S. Wrighton, *Chem. Mater.*, 1995, **7**, 418.