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Facile Reduction of Poly(2,5-dialkoxy-*p*-phenylene ethynylene)s: An Efficient Route for the Synthesis of Poly(2,5-dialkoxy-*p*-xylylene)s

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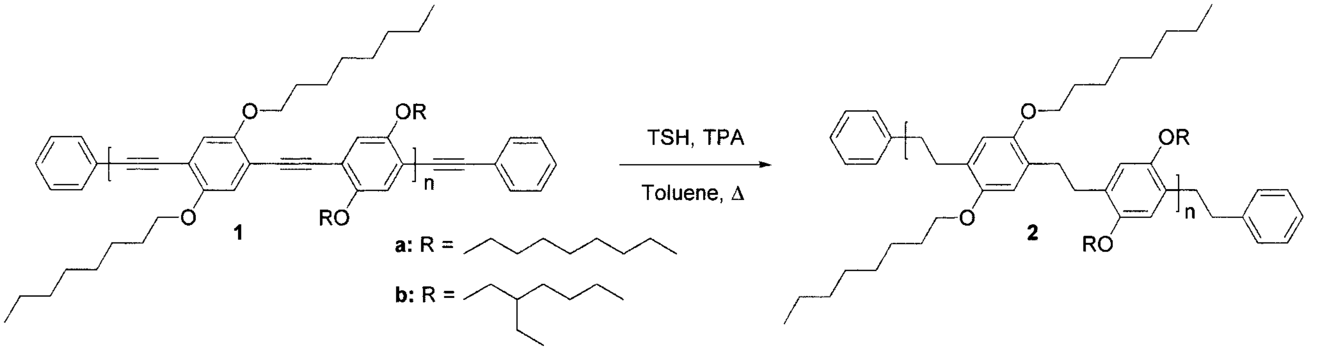
In a recent communication, Bunz and co-workers[1] have demonstrated for the first time that conjugated poly(*p*-phenylene ethynylene) (PPE) derivatives can be reduced to the corresponding poly(*p*-xylylene)s (PPX) under catalytic hydrogenation conditions. While this finding may initially seem trivial, the reduction of the triple bonds in PPEs has proven to be unexpectedly challenging,[1] and as a result, no successful hydrogenation of these materials had been reported prior to Bunz's work. The ability to reduce such ethynylene units is, however, rather important, since it imparts the possibility to decrease the conjugation length in these photo-[2] and electroluminescent[3] polymers, thus allowing easy tuning of their photophysical characteristics. Furthermore, the availability of an efficient protocol for the full hydrogenation of PPE derivatives and related nonconjugated ethynylene-containing arylene alkylene polymers, which have also proved to be difficult to reduce,[4] may open up an alternative synthetic route to poly(arylene alkylene)s.[5] PPX, the most prominent representative of this class of polymers[6] (which feature only alkyl and aromatic units in the backbone), offers a unique matrix of excellent characteristics, including outstanding thermal and mechanical properties, good solvent resistance, low dielectric permittivity, high crystallinity, and bulk barrier properties which are among the best of organic polymeric coatings.[7,8] However, on account of the intractability of PPX, much interest has focused on more processable members of this family of materials.[5,7] Representative examples include derivatives with solubilizing substituents on either the aromatic ring or the ethylene unit[9] or extended aliphatic segments in the backbone.

Unfortunately, Bunz observed that, in order to fully reduce poly(2,5-dialkyl-*p*-phenylene ethynylene)s by catalytic hydrogenation with Wilkinson's catalyst, rather drastic conditions have to be employed. The latter include the use of extreme temperatures (350 °C), high hydrogen pressures (350−510 bar), and long reaction times (75−132 h).[1] These harsh conditions may limit the general applicability of this synthetic framework; for example, at such temperatures the frequently utilized 2,5-dialkoxy derivatives[2,10−12] of poly(*p*-phenylene ethynylene)s are expected to decompose.[13] This situation prompted us to revisit the hydrogenation of PPEs, and in particular poly(2,5-dialkoxy-*p*-phenylene ethynylene)s, to the corresponding poly(*p*-xylylene) (PPX) derivatives. We, therefore, turned our attention to the diimide reduction method developed by Hahn,[14] which has proved versatile in the reduction of a number of unsaturated polymers and has been tailored to eliminate side reactions.[15] This method involves reacting the polymer with *p*-toluenesulfonhydrazide (TSH) and tripropylamine (TPA) in hot toluene and can be conveniently performed under mild conditions. While diimide chemistry has been used to hydrogenate low-molecular-weight alkynes,[16] surprisingly, this method—to our best knowledge—hitherto has not been employed for the reduction of ethynylene-containing polymers.

To examine the potential of this synthetic framework in context of ethynylene-containing polymers, we first subjected poly[1,4-(2,5-dioctyloxyphenylene)ethynylene] (O-OPPE, **1a**), a PPE derivative with well-documented photo- and electroluminescent properties,[12] to the diimide reduction conditions (Scheme 1), which one of us had successfully used before for the reduction of nonconjugated, double-bond-containing polymers.[17] The procedure employed here represents a modification of the original protocol,[14] as the reactions were conducted with off-the-shelf reagents in an open reaction vessel and used hot toluene as the solvent. In view of the notorious stability of the conjugated triple bond in PPE derivatives (vide supra), a large excess of the reagents TSH and TPA was added in two portions. After standard workup, a very pale yellow powder was isolated in good yield. The material was found to be highly soluble in a variety of solvents, including chloroform and warm toluene. Gratifyingly, ^{1}H and ^{13}C NMR spectra are consistent with the structure of the fully reduced

Scheme 1. Hydrogenation of Poly[1,4-(2,5-dioctyloxyphenylene)ethynylene] (O-OPPE, 1a) and Poly[2,5-dioctyloxy-1,4-diethynylphenylene-*alt*-2,5,-bis(2′-ethylhexyloxy)-1,4-phenylene] (EHO-OPPE, 1b) with *p*-Toluenesulfonhydrazide and Tripropylamine in Hot Toluene, Yielding Poly[1,4-(2,5-dioctyloxyphenylene)xylylene] (2a) and Poly[2,5-dioctyloxy-1,4-diethylphenylene-*alt*-2,5,-bis(2′-ethylhexyloxy)-1,4-phenylene] (2b), Respectively



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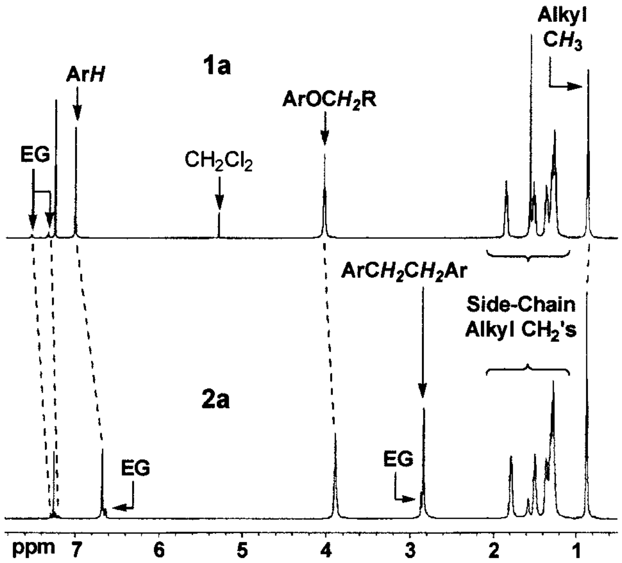

Figure 1. ^{1}H NMR spectra of poly[1,4-(2,5-dioctyloxyphenylene)ethynylene] (O-OPPE, **1a**) and poly[1,4-(2,5-dioctyloxyphenylene)xylylene] (**2a**) measured at 600 MHz in $CDCl_3$. EG refers to resonance peaks corresponding to end groups.

polymer **2a** and suggest that the ethynylene moieties of **1a** have been completely hydrogenated. Figure 1 shows the ^{1}H NMR spectrum of starting material **1a** and product **2a**. Both spectra nicely reflect the presence of phenyl end groups (confirmed by HMQC experiments), which were introduced to control the molecular weight of the original PPE derivative **1a**. Integration of the latter signals allows elucidation of the degree of polymerization (DP) of **1a** (DP ~ 21, corresponding to a number-average molecular weight M_n of ca. 7500) and the resulting **2a** (DP ~ 17, M_n of ca. 6500). The comparable M_n suggests the absence of extensive chain cleavage of the polymer upon reduction. This finding is corroborated by GPC data, which reveal an M_n of ca. 16 000 with a polydispersity of 5.3 for the starting material **1a** and an M_n of ca. 15 000 with a polydispersity of 5.8 for the resulting **2a**. (Note, however, that the molecular weights determined from the GPC experiments were calibrated against polystyrene standards, and as a consequence of the rigid nature of the polymers under consideration, these values are considerably higher than those obtained by NMR end-group analysis.) Other than the appearance of a resonance around 2.77 ppm, corresponding to the new $\mathrm{Ar{-}C}H_2\mathrm{{-}C}H_2\mathrm{{-}Ar}$ moieties, a smaller signal at 2.80 ppm is observed, which we assign to the methylene units connected to the phenyl end groups (again based on HMQC data). The signal of the aromatic protons experiences a shift to lower field upon reaction, reflecting the reduction of the electron-withdrawing ethynylene units. The similarity of the integrals of the diagnostic methylene units ($\mathrm{OC}H_2$ and $\mathrm{Ar{-}C}H_2\mathrm{{-}C}H_2\mathrm{{-}Ar}$) and the absence of the aromatic signal characteristic of the starting material indicates complete conversion to **2a**.

The faint pale yellow color of the product and the fact that the elemental analysis data slightly deviated from the expected values prompted us to do a control experiment and submit **2a** to a second hydrogenation. The material thus obtained showed slightly better microanalytical data; however, the slight coloration persisted, and NMR spectra appeared identical to those obtained for the original **2a**. Analytical data for S and N indicate that the presence of these elements is below 0.1 and 0.25%, respectively, suggesting that the level of standard defects arising from TSH degradation (cf. below) is well below 1 mol %, even in this initial, unoptimized procedure. It should be noted that the elemental analysis remained essentially unchanged upon further reprecipitation, suggesting that the minor amount of contamination is *not* a low-molecular-weight byproduct. A detailed inspection of the aromatic region of the 1D and HMQC spectra (cf. Supporting Information) of this polymer revealed the absence of olefinic proton signals, which would be expected if partial hydrogenation resulted in the formation of double bonds.[18] Further, also FT-IR spectra (Supporting Information) suggest the absence of residual olefinic moieties in the reduced polymers, although the spectra are somewhat noisy in the diagnostic region. We should also note in this context that high-resolution (600 MHz) ^{1}H NMR spectra of polymer **2a** after the first and second reduction demonstrate that the typical side products that can occur in TSH chemistry (e.g., $\mathrm{H_3C{-}Ar{-}S{-}R}$, leading to a singlet at around 2.4 ppm)[14] are absent, and no other unaccountable signals are detected. Furthermore, FT-IR spectra (Supporting Information) are void of a band at 1090 cm^{-1}, which corresponds to the Ar−C−S− stretch and is indicative for the presence of aryl sulfides or aryl sulfones. Thus, while the elemental analysis suggests a minor amount of impurity, the combination of high-resolution ^{1}H NMR and FT-IR is unable to account for the latter.

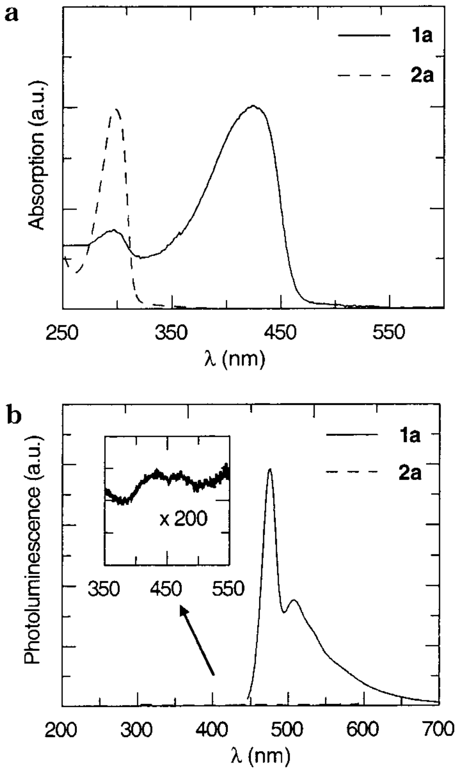

Figure 2. UV−vis absorption (a) and photoluminescence (b) spectra of poly[1,4-(2,5-dioctyloxyphenylene)ethynylene] (O-OPPE, **1a**), solid line, and poly[1,4-(2,5-dioctyloxyphenylene)xylylene] (**2a**), dashed line, in $CHCl_3$. The inset in (b) displays the emission of **2a** with a 200-fold amplification. PL emission spectra were obtained under excitation at the wavelength of maximum absorption.

We subsequently turned our attention to the optical characteristics of the original **2a**. Figure 2 shows the UV/vis absorption and photoluminescence spectra of this material, in comparison to those of the parent PPE derivative **1a**. Upon reduction, the strong absorption band related to the $\pi-\pi^*$ transition of the conjugated polymer backbone completely disappeared. The spectrum reveals a strong absorption band centered around 298 nm, and the polymer is essentially transparent at wavelengths above 350 nm. The disruption of the extended π-conjugated system upon hydrogenation is also apparent in the steady-state photoluminescent spectrum of the polymer (Figure 2b). While **1a** is highly fluorescent and shows a diagnostic, well-structured emission spectrum in the green regime,[12] PL emission spectra of **2a** recorded under conditions that allow a direct comparison of the intensity with the one of **1a**, as expected, reveal only a very weak and featureless emission.

We also applied the diimide hydrogenation protocol to poly[2,5-dioctyloxy-1,4-diethynylphenylene-*alt*-2,5-bis(2′-ethylhexyloxy)-1,4-phenylene][12] (EHO-OPPE, Scheme 1, **1b**), a more soluble structural isomer of **1a** featuring sterically hindered 2-ethylhexyl groups. Gratifyingly, also in this case, ^{1}H and ^{13}C NMR spectral data as well as chemical composition determined by elemental analysis are consistent with the structure of the reduced polymer **2b**. The photophysical characteristics of this polymer were found to be essentially identical with those of **2a**, reflecting the rather similar chemical structure of these two polymers.

DSC experiments and polarized microscopy revealed that **2a** and **2b** unequivocally are of semicrystalline nature. As expected, the hydrogenation reduces the rigidity of the polymer backbone, resulting in lower thermal transition temperatures when compared to the starting materials. While the parent PPEs **1a** and **1b** display glass transition temperatures around 100 °C and do not melt before thermal decomposition sets in at around 150 °C,[12,13] the DSC trace of **2a** reveals a sharp endothermic peak at 170 °C, associated with the melting of this polymer. The DSC melting endotherm of **2b** centered around 135 °C was observed to be slightly broader than the one of **2a**, but the melting enthalpies indicate similar degrees of crystallinity for the two materials. The semicrystalline character of the new PPX derivatives **2** is, from an engineering point of view, very desirable.[5,7] However, rather surprisingly, this morphological feature is in contrast to the amorphous nature reported by Bunz for a series of poly[1,4-(2,5-dialkylphenylene)xylylene]s of very similar chemical structure.[1] The reason for this discrepancy is presently unclear, but it should be noted that the latter polymers were of substantially higher molecular weight than the materials investigated here.

Thus, in summary, we have demonstrated that diimide generated from *p*-toluenesulfonhydrazide and tripropylamine is a convenient and very effective reagent for the hydrogenation of PPEs under mild and undemanding conditions. In our initial experiments presented here, this protocol was employed to reduce two different PPE derivatives to the corresponding poly(*p*-xylylene)s. In contrast to the underivatized PPX, which is rather intractable,[7] the polymers prepared here are readily soluble in a variety of organic solvents. Furthermore, these new polymers are of semicrystalline nature, but as a consequence of the side-chain derivatization, their melting temperatures are substantially reduced when compared to PPX. Clearly, the low degree of polymerization of the samples employed in the present model study limits many of the relevant materials characteristics. Thus, to elucidate the property matrix of these new hydrocarbon polymers in detail, a more systematic study of this particular family is currently being pursued. Considering the difficulties experienced in previous attempts to hydrogenate the conjugated ethynylene moieties in PPEs, it can be speculated that the methodology employed here should also be applicable to other (nonconjugated) ethynyl-containing macromolecules, and we envision that this approach can be readily extended to a variety of polymer systems. Finally, it should be noted that in the attempt to achieve complete hydrogenation, all reactions conducted in this study employed precautionary long reaction times and large excesses of the reducing agent. However, these conditions have not been optimized, and the investigation of the influence of the various reaction parameters on the hydrogenation efficiency will be the subject of further studies.

Experimental Section. All chemicals were used as received. Phenyl end-capped O-OPPE (**1a**) and EHO-OPPE (**1b**) of a number-average molecular weight of approximately 7500 g mol^{-1} (DP $\sim$ 21) were prepared as described before.[12] DSC traces were recorded under a nitrogen atmosphere on a Perkin-Elmer DSC Pyrus 1 on once-molten samples at heating and cooling rates of 10 K/min. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 800, and PL spectra were measured on a SPEX Fluorolog 3 (model FL3-12). ^{1}H NMR and ^{13}C NMR spectral data are expressed in ppm relative to internal TMS and were obtained on a Varian 600 MHz NMR spectrometer. GPC data were calibrated against polystyrene standards and collected on a Varian Prostar equipped with a model 350 RI detector and a model 320 UV/vis detector and employing a Waters Styragel HR4E column and $CHCl_3$ as the eluent. Elemental analyses were carried out by Oneida Research Services Inc.

Reduction of 1a. To a solution of O-OPPE (**1a**) (218 mg, 0.611 mmol) in hot toluene (25 mL) was added *p*-toluenesulfonhydrazide (TSH) (1.14 g, 6.11 mmol) and tripropylamine (TPA) (0.878 g, 6.13 mmol). The mixture was heated at reflux for 90 min. Another portion of TSH (1.15 g, 6.16 mmol) and TPA (0.90 g, 6.3 mmol) was added, and the mixture was stirred under reflux for a further 2 h. The pale yellow mixture was filtered hot through an alumina plug, which was subsequently washed with hot toluene. The combined organic layers were washed with water (2 × 10 mL), and the organic solution was precipitated into methanol. The resulting solid was filtered off, washed with methanol, and dried in vacuo to yield poly[1,4-(2,5-dioctyloxyphenylene)-xylylene] (**2a**) as a very pale yellow powder. The polymer was reprecipitated by addition of a $CHCl_3$ solution into methanol, yielding a faint yellow solid (147 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.32−7.16 (m, 5H/end group, Ph end group), 6.70−6.61 (s, 4H, ArH), 3.89 (m, 8H, OCH_2), 2.80 (s, Ar−CH$_2$−CH_2−Ph end group), 2.77 (s, 8H, Ar−CH_2−CH_2−Ar), 1.82−1.76 (m, 8H, CH_2), 1.52−1.46 (m, 8H, CH_2), 1.40−1.22 (m, 32H, CH_2), 0.87 (t, $^3J_{(H,H)} = 6.9$ Hz, 12H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ 150.9 (C_{Ar}−O−R), 129.5 (C_{Ar}−CH$_2$−CH$_2$), 128.7, 128.5 (both Ph end group), 114.5 (C_{Ar}−H), 69.1 (O−CH$_2$−R), 37.0, 33.2 (both Ar−CH_2−CH_2−Ph end group), 32.1 (CH$_2$), 31.5 (CH$_2$−Ar), 30.0, 29.7, 29.6, 26.5, 22.9 (all CH$_2$), 14.3 (CH$_3$). DP = 17 (^{1}H NMR). Anal. Calcd for $C_{422}H_{694}O_{34}$ (based on a DP of 17): C, 80.30; H, 11.08. Found: C, 78.01; H, 9.91; N, 0.06. T_m = 170 °C, T_{cryst} = 145 °C.

A sample of **2a** was subjected to a second reduction employing reaction conditions that were identical to the ones outlined above. However, only 1 portion of TSH and TPA (10 equiv, each) was added, and a reaction time of 5 h was applied. Rereduced **2a** of similar appearance was obtained in a yield of 88%, exhibiting ^{1}H and ^{13}C NMR spectra identical to the sample that was only reduced once. Anal. Calcd for $C_{422}H_{694}O_{34}$ (based on a DP of 17): C, 80.30; H, 11.08. Found: C, 78.93; H, 10.90; N, 0.23; S, 0.09. A small amount of the sample was reprecipitated as described above. Anal. Calcd for $C_{422}H_{694}O_{34}$ (based on a DP of 17): C, 80.30; H, 11.08. Found: C, 78.94; H, 11.05; N, 0.35; S, 0.08.

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Supporting Information Available: Experimental details for the synthesis of **2b**, including ^{1}H and ^{13}C NMR, UV−vis absorption, and photoluminescence spectra; FT-IR spectra of **1a** and **2a**; and enlargements of the high-resolution ^{1}H NMR data of **2a** including enlargements of the aromatic region of the 1D and HMQC spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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