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Rod vs Coil: Molecular Weight Comparison of a Poly(dialkyl-*p*-phenyleneethynylene) with Its Reduced Poly(2,5-dialkyl-*p*-xylylene)

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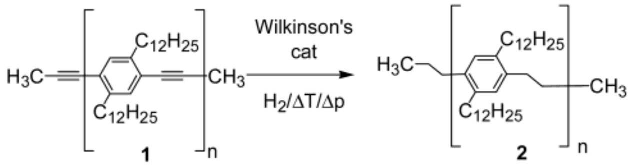

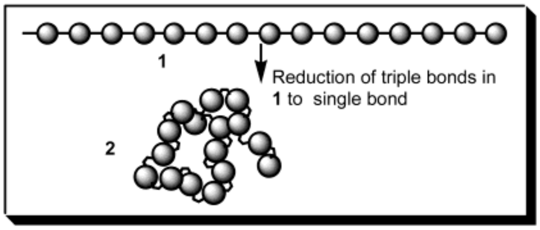

In this communication we report the correlation of the apparent molecular weight of poly(*p*-phenyleneethynylene)s (PPE, **1**) to that of their reduced congeners, the poly(*p*-xylylene)s (**2**), as determined by gel permeation chromatography (GPC).[1,2] We find that the apparent molecular weights of the reduced polymers **2** are lower by a factor of 1.42 when compared to those of the PPEs due to the increased flexibility of **2** compared to **1**.[3]

Determination of absolute molecular weights of rigid-rod polymers is not trivial,[4,5] and the most common characterization method, gel permeation chromatography (GPC), exaggerates their molecular weights. Tour[6] examined large oligomeric PEs. Their molecular weight is overestimated by a factor of $\approx$2 if examined by GPC. For higher molecular weight PPEs (HPPE), that factor seems to decrease as Cotts and Swager[7] have found by light scattering: HPPEs are not linear-rigid anymore but somewhat flexible. However, light scattering gives reliable size information that is related to M_w and not to M_n. It does not inherently address polydispersity issues satisfactorily; highly fluorescent and aggregating samples such as PPEs pose further challenges. MALDI−TOF is an option but is unreliable for polymers with broad molecular weight distributions.[4] In addition, MALDI of conjugated polymers suffers from molecular-weight-dependent change of cross section of ionization which further complicates matters.[4] A convenient way to determine the absolute molecular weight of PPEs is therefore not readily available.[5] An elegant solution of this problem would be the conversion of rigid rods into floppy coils by a polymer analogous reaction. Postpolymerization processes are challenging because high yields and specificity are prerequisites for the synthesis of molecularly defined materials. PPEs **1** (available on a g-scale by ADIMET)[3,8] offer a unique opportunity because hydrogenation of the triple bonds transforms rod **1** into coil **2** without appreciable increase in molecular weight, but with a substantial increase in flexibility. Under forcing conditions (Wilkinson's catalyst, 300 °C, 72 h, 475 atm of H_2, Parr bomb) **1** is cleanly hydrogenated into **2** and isolated in high yield and purity as a colorless solid.[1] According to NMR spectroscopy, **2** does not show defect structures or overhydrogenation (spectra are displayed in ref 1). *With the successful hydrogenation of* ***1*** *→* ***2*** *a chemical rod−coil transformation is available to systematically determine physical differences between a rod and a coil of the exact same degree of polymerization* (P_n). We have thus a simple way to obtain more accurate, GPC-based molecular weights for PPEs **1** via **2**, because **2** is more flexible and thus more amenable to molecular weight determination by GPC. We would use pairs of PPEs and **2** to construct a relationship between the hydrodynamic volume (i.e., GPC values) of a rigid rod and a coil of the same P_n. The apparent molecular weight of PPEs is proportional to the polymerization time of the dipropynyl(dialkyl)benzenes used to make **1**, so we can manipulate the "apparent" P_n in **1**.[8] We have prepared a series of didodecyl-PPEs of different molecular weights and hydrogenated all of them into **2**.[9] Plotting the obtained peak molecular weights MW_{peak} **1** vs MW_{peak} **2** should lead to a curve that links the apparent molecular weight of PPEs to the apparent molecular weight of **2**. The following relationship should hold: MW_{peak} PPE = ωMW_{peak} **2**. While long PPEs are not rigid (high P_n), they may behave as wormlike chains according to the Kratky−Porod model.[10] The PPX **2** are extremely well soluble in hexanes, toluene, and nonpolar solvents. Figure 1 shows the dependence of the melting temperature upon the molecular weight of the PPEs and the PPXs of identical degree of polymerization. The difference between the melting points of PPE **1** and the reduced PPX **2** is variable. The PPX melt on average 18 °C lower, suggesting a lower order in **2**. These results are in good agreement with the observations of Weder et al.,[2] who examined the reduction of dialkoxy-PPEs and reported the thermal behavior of several dialkoxy-PPXs.

Figure 2 shows the results of a series of bomb reduction experiments of **1** into **2**. All of the samples of **1** and of **2** were examined by GPC vs polystyrene.[9] The GPC data were processed by plotting the peak molecular weights (MW_{peak}) of **2** (X-axis) vs MW_{peak} of **1** (Y-axis). A linear regression allows the molecular weight correlation to be formulated as MW_{peak} **1** = $1.42 MW_{peak}$ **2**; i.e., the molecular weight of the PPEs is overestimated in comparison to that of the reduced polymers **2** by a factor of 1.42. Attempts to fit/correlate the data either to a log scale or to a polynomial gave less satisfying results.

The slope of 1.42 is lower than the factor of 1.97 (obtained by dividing M_n from GPC by the true molecular weight (MW)) that was reported by Tour[6] for medium-sized phenyleneethynylene oligomers. These are the most exact *absolute* values available for PEs. The relatively moderate differences in the molecular weights between **1** and **2** is surprising in light of Tour's

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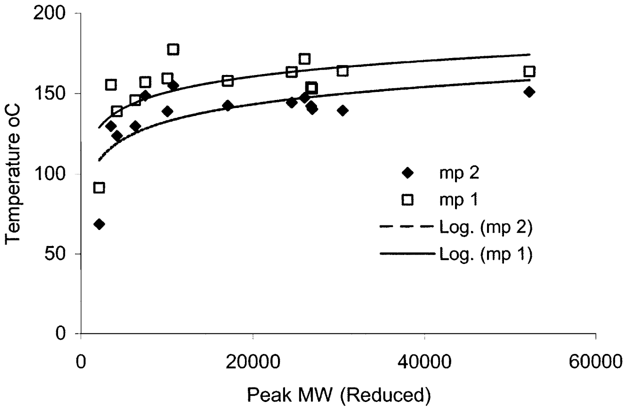

Figure 1. Comparison of the melting points (DSC) of polymers **1** and **2**. The melting points of the reduced polymer are on average 18 °C (8–25 °C) lower than that of the PPE **1**. The melting points of the polymers are dependent upon the molecular weight of the polymers under consideration.

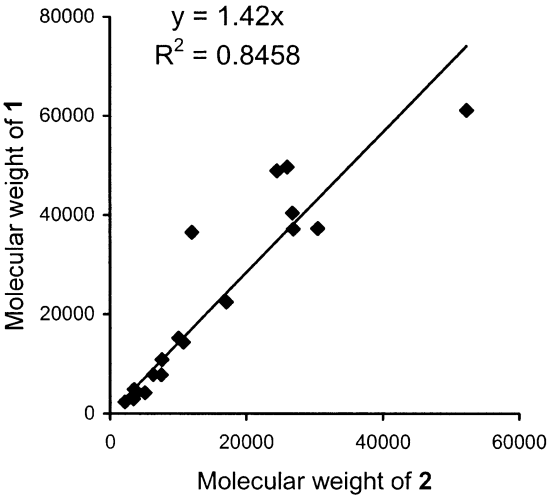

Figure 2. Comparison of the molecular weight obtained by gel permeation chromatography of **1** and **2**. The *X*-axis is defined by the molecular weight of **2**, and the *Y*-axis is defined by the molecular weight of **1**. The best fit of the molecular weight data is a linear correlation with a slope of 1.43.

results but well in line with Cotts and Swager's light scattering studies on PPEs.[7] According to Cotts,[7] PPEs are quite flexible macromolecules with a persistence (Kuhn) length of 40 phenyleneethynylene repeating units (30 nm). Our GPC results are in qualitative accord with the light scattering study by Cotts, pointing out that PPEs are not rigid rods but probably wormlike chains in dilute solution.[10,11]

In conclusion, we have demonstrated that the reduction of PPEs **1** turns "rigid rods" into more "floppy coils". We have compared the apparent peak molecular weights (GPC) of the didodecyl-PPEs **1** to those of their reduced congeners **2**. We find that the polymers **2** have a molecular weight that is—on the average—a factor of 1.42 lower than that of **1**. The reduced polymers, the PPX, are nonabsorbing and nonfluorescent. They are excellent candidates for future light scattering studies to further probe molecular weight issues in these interesting systems.

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Supporting Information Available: A table with all molecular weight data and polydispersities. This material is available free of charge via the Internet at http://pubs.acs.org.

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