4688 *Macromolecules* **2001,** *34,* 4688−4690

Alkyne-Bridged Polymers as Platform for Novel Macromolecular Materials: Catalytic Hydrogenation of Poly[(*p*-dialkylphenylene)ethynylene]s

Alan R. Marshall and Uwe H. F. Bunz*

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208

Received April 2, 2001
Revised Manuscript Received May 14, 2001

We describe the hydrogenation of poly(*p*-phenyleneethynylene)s (PPE, **1**) to their fully hydrogenated counterparts, the poly(*p*-phenyleneethylene)s (**2**). Complete hydrogenation was achieved utilizing Wilkinson's catalyst under drastic conditions (75 h, 520 bar of H_2, 300 °C).

Alkyne metathesis with simple catalyst systems allows the synthesis of dialkyl-PPEs **1** of high molecular weight and purity.[1] The facile access to high-quality PPEs makes **1** an attractive candidate for polymer analogous reactions. Starting from **1**, a host of different and novel polymeric architectures should be accessible by conversion of the C≡C triple bond. Chemical derivatization of conjugated polymers is an important topic, and recently Holdcroft[2] reported the successful halogenation and nitration of polythiophenes. On the other hand, Scherf[3] has utilized sophisticated postfunctionalization schemes to access ladder polymers from poly(*p*-phenylene)s. However, postfunctionalization of PPEs has been conspicuously absent from the literature, with the exception of Yamamoto's report of HBr addition to thiophene-containing poly(aryleneethynylene)s[4] and Swager's ladder polymer synthesis.[5] Successful hydrogenation of poly(aryleneethynylene)s has not been reported, despite the great interest, which poly(*p*-xylylene)s[6]/poly(*p*-phenyleneethylene)s[7] hold for application in high-temperature materials. We are interested in the development of reliable polymer analogous reactions for PPEs and report hydrogenation of **1** as a step into that direction.

In a first attempt, we performed homogeneous hydrogenation of PPE **1a** at a temperature of 200 °C and under a pressure of 100 bar for 24 h with 5 mol % of Wilkinson's catalyst $(Ph_3P)_3RhCl$ in toluene. Workup recovered a deep yellow polymer, in which some (NMR spectroscopy) triple bonds were hydrogenated to double bonds, but which according to UV−vis spectroscopy was still fully conjugated. An attempt to reduce PPEs by diborane in toluene failed and led to the isolation of an insoluble and uncharacterizable, but colorless, material. From the partial hydrogenation of PPEs (vide supra), we concluded that under more forcing conditions we might be able to convert PPEs into their saturated congeners **2**. Indeed, increasing the reaction temperature to 300 °C under a pressure of 500 bar of H_2, utilizing again toluene as solvent and $(Ph_3P)_3RhCl$ as catalyst, furnished the hydrogenated poly(*p*-dialkylphenyleneethylene)s **2a**−**d** from **1a**−**d** in almost quantitative yield as *colorless* solids after filtration and precipitation into methanol. In one experiment the pressure reaction was terminated after 6 h at 300 °C and 500 bar of H_2, to afford only partially reduced and distinctly yellow polymers. This experiment strongly supports the notion that the harsh reaction conditions described herein are not an "overkill" but necessary to achieve complete hydrogenation. The reason for the low reactivity of the PPEs toward the conditions of catalytic hydrogenation is probably the encumbered steric environment brought along by the four alkyl groups, which surround the diphenylalkyne units in **1**. From our own preliminary experiments we know that hydrogenation becomes much more difficult when going from diphenylacetylene to the PPEs. In addition, there may be a significant effect of the large conjugated π-electron system, which could likewise diminish the reactivity of the PPEs by lowering both HOMO and LUMO.

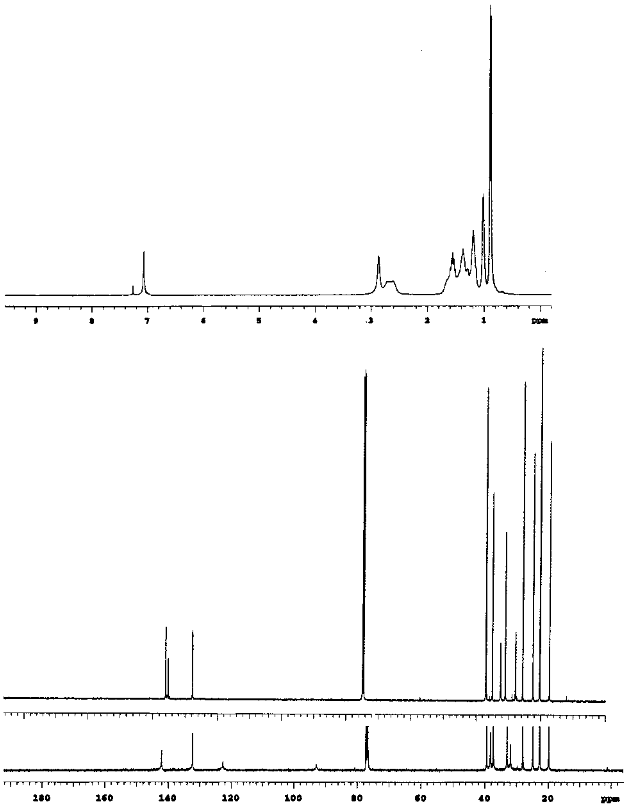
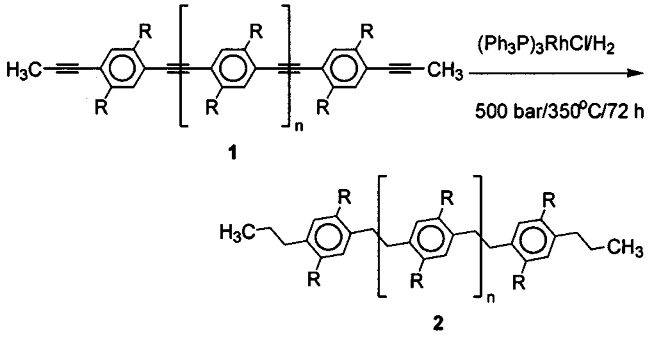


Figure 1. (a, top) ^1H NMR spectrum of **2a** in $CDCl_3$. The signal at 7.24 ppm is due to residual $CHCl_3$ in the utilized $CDCl_3$. (b, bottom) ^{13}C NMR spectrum of polymer **2a** (top) overlaid to the ^{13}C NMR spectrum of polymer **1a** (bottom). Both spectra are taken in $CDCl_3$ (signal at 77 ppm), and the intensities of signals of the alkyl group in **1a** are cut off for clarity.

Scheme 1



10.1021/ma010557e CCC: $20.00

Table 1. Reduction Experiments and Substituent Key for 1 and 2

R	key	mg of **1**	mmol	mg of cat.	mmol	mL of C_7H_6	rxn time (h)	p (bar)	% yield of **2**
3,7-dimethyloctyl	a	300	0.788	30	0.0324	3	75	350	91
dodecyl	b	500	1.14	50	0.0540	5	75	510	92
dodecyl	b	160	0.366	15	0.0162	3	75	360	94
dodecyl	b	300	0.687	30	0.0324	4	132	415	78
2-ethylhexyl	c	250	0.770	25	0.027	3	75	470	90
nonyl	d	350	0.992	35	0.037	4	75	480	93

All of the polymers **2a**−**d** are colorless, amorphous, and non-liquid-crystalline solids,[1d] well soluble in chloroform and dichloromethane, while the starting materials are hardly soluble, yellow, and crystalline polymers. Table 1 shows results of six different reduction experiments. The ^{1}H and ^{13}C NMR spectra of **2a** (R = (S)-3,7-dimethyloctyl) are shown in Figure 1. In the ^{1}H NMR spectrum of **2a** the signal due to the aromatic protons has shifted from $\delta = 7.4$ to 7.1 ppm upon reduction. In addition, a narrow singlet at $\delta = 2.9$ ppm emerges, which is due to the newly formed $-CH_2-CH_2-$ groups, and the broad doublet of the benzylic protons of the side chains has shifted upfield by 0.1 ppm from 2.75 to 2.66 ppm. In the ^{13}C NMR spectrum of **2a**, which is overlaid with the ^{13}C NMR spectrum of **1a**, the signal for the alkyne groups has disappeared, and the signals of the aromatic carbons have experienced a significant downfield shift. In the alkyl region, where there would be 11 bands expected, 10 are recorded. According to a C−H correlation experiment, the signals of the benzylic carbons of the side chains as well as the signal of the 1,2-ethanediyl group show accidentally the same chemical shift. That explains the apparent lack of the 11th resonance with the four benzylic CH_2 carbons resonating at $\delta = 39.6$ ppm. In addition, the characteristic peak for the alkyne unit in the spectrum of **1a** has disappeared completely upon hydrogenation. The recorded spectroscopic data are in excellent agreement with the proposed structure of **2**. To show that backbone hydrogenolysis, i.e., degradation of the polymer, is not a problem, we overlaid the GPC traces of **1a** and **2a** in Figure 2. While the peak molecular weight decreases by approximately 10% in **2a**, the polydispersity (PDI) likewise decreases from PDI = 3.7 to 3.2. The general shape and appearance of the GPC trace stays the same (see Figure 2), suggesting that if we have backbone hydrogenolysis, it must be a minor process. The conversion of **1** into **2** is at the same time a chemical rod−coil transformation.[8] The small difference in the molecular weights between **1a** and **2a** is noteworthy and seems to suggest that PPEs are quite flexible, in accord with the light scattering experiments done by Cotts and Swager.[8] In the future we will analyze a series of different PPEs of different molecular weights and corroborate this trend.

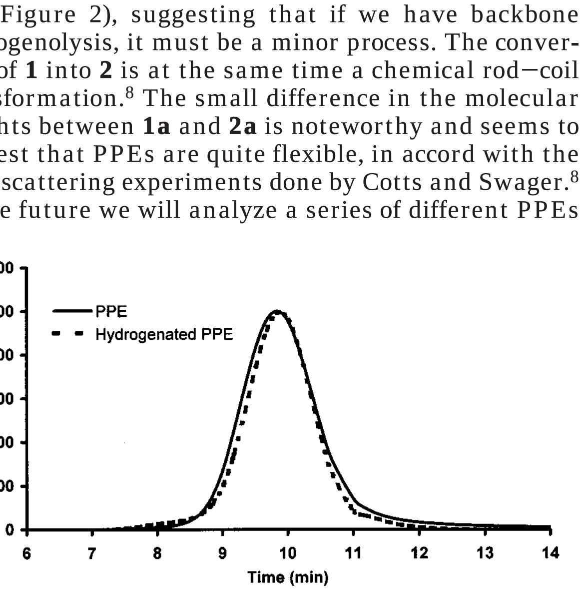


Figure 2. Overlaid GPC traces of the starting PPE **1a** (P_n = 91, PDI = 3.7, P_{peak} = 157) and the reduced dialkylpoly-p-xylylene **2a** (P_n = 92, PDI = 3.2, P_{peak} = 143).

In conclusion, we have shown that PPEs **1a**−**d** are amenable to polymer analogous hydrogenation, and Rh-catalyzed reduction furnishes the hydrogenated poly(dialkyl-p-xylylene)s **2** in excellent yield and high purity. The significance of this work is beyond the synthesis of a novel polymer by reduction of PPEs. Our findings suggest that transition-metal-catalyzed processes can efficiently transform PPEs into other structures despite the extreme conditions necessary to coax these unreactive substrates. The fact that hydrogenation works for PPEs encourages to search for other reactions which will transform PPEs into a host of novel and interesting materials, otherwise difficult or impossible to obtain. The hydrosilylation, hydrocyanation, and hydroformylation reactions of PPEs are currently under investigation.

Experimental Section: Synthesis of 2a. A stainless steel pressure bomb (Parr systems, capable to withstand 690 bar at 350 °C, equipped with a burst disk for 550 bar; volume 77 mL) is charged with **1a** (300 mg, 0.788 mmol of GPC (polystyrene standard), $P_n = 91$, PDI ($M_w/M_n = 3.7$, $P_{peak} = 157$), prepared according to ref 1c and used as obtained after ^{1}H NMR and ^{13}C NMR spectroscopic characterization), Wilkinson's catalyst ($(Ph_3P)_3RhCl$, 30 mg, 32.4 μmol), and toluene (3 mL). The bomb is cooled with liquid N_2 to 77 K and charged from a hydrogen bomb to 130 bar of H_2. The cooling bath is removed, and the bomb is allowed to warm to room temperature. Then the bomb is put into a tailor-made brass heating block and heated to 300 °C for 75 h. After cooling to ambient temperature, the pressure is carefully released, and the reaction mixture is diluted by chloroform (50 mL). Filtration removes elemental Rh. The clear colorless solution is precipitated into methanol and refrigerated for 18 h. Collection of the precipitated polymer is followed by drying in high vacuum (50 °C, 2 h) to furnish **2a** (276 mg, 91%). ^{1}H NMR ($CDCl_3$): δ = 7.06 (s, 2H), 2.87 (s, 4H), 2.66 (bs 4H), 1.55 (bm, 8H), 1.36 (bm, 8H), 1.19 (bm, 4H), 1.00 (d, 6H) 0.97 (d, 12H). ^{13}C NMR ($CDCl_3$): δ = 138.63, 137.86, 130.38, 39.63, 37.60, 35.05, 33.61, 30.46, 28.25, 25.10, 23.00, 22.90, 19.99 IR (KBr): v = 2956, 2867, 1501, 1473, 1384 cm^{-1}. GPC: $P_n = 92$, $P_{peak} = 143$, PDI = 3.2. Molecular weight determination was performed by gel permeation chromatography with polystyrene as standard.

Acknowledgment. We thank the National Science Foundation (CHE 9814118) and the Petroleum Research Funds for generous funding. We thank Winfried Steffen for a sample of **1a** and Dr. Ruta Bly for a sample of **1c**.

References and Notes

(1) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1998**, *120*, 7973. (c) Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194. (d) Kloppenburg, L.;

Jones, D.; Claridge, J. B.; zur Loye, H. C.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4460.

(2) Li, Y.; Vamvounis, G.; Holdcorft, S. *Macromolecules* **2001**, *34*, 141.

(3) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489. Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.

(4) Yamaoto, T. *Chem. Lett.* **1993**, 1959. Yamaoto, T.; Yamada, W.; Takagi, M.; Kizu, K.; Maruyamata, T.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K. *Macromolecules* **1994**, *27*, 6620.

(5) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

(6) Greiner, A.; Mang, S.; Schäfer, O.; Simon, P. *Acta Polym.* **1997**, *48*, 1. Greiner, A. *Trends Polym. Sci.* **1997**, *5*, 12. Schäfer, O.; Greiner, A. *Macromolecules* **1996**, *29*, 6074. Wege, V. U.; Greiner, A. *Acta Polym.* **1995**, *46*, 391.

(7) For an excellent review, see: Steiger, D.; Tervoort, T.; Weder, C.; Smith, P. *Macromol. Rapid Commun.* **2000**, *21*, 405.

(8) Cotts, P. M.; Swager, T. M.; Zhou, Q. *Macromolecules* **1996**, *29*, 7323.

MA010557E