Paracyclophene Route to Poly(*p*-phenylenevinylene)

Yi-Jun Miao and Guillermo C. Bazan*

Department of Chemistry, University of Rochester
Rochester, New York 14627

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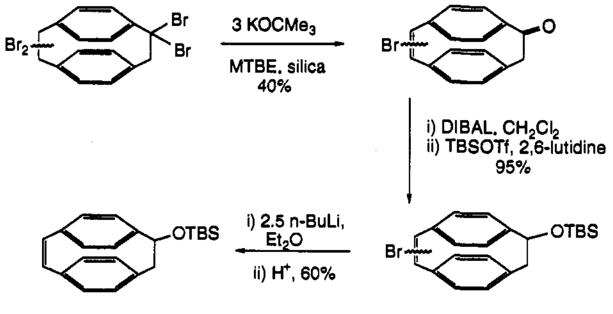
There is significant current attention focused on poly(*p*-phenylenevinylene) (PPV) in view of the material's performance as the electroluminescent component in devices relevant for new technologies. In addition, unraveling the intricate relationship between structure and photooptical properties in PPV furthers our understanding of the organic solid state.[1] The development of efficient and versatile synthetic routes to this material using precursor polymers has proven critical to the progress of this effort. The most widely used synthesis remains the water-soluble sulfonium polyelectrolyte approach of Wessling and Zimmerman, which produces high molecular weight PPV *via* mild thermolysis of precursor polymer.[2] However, since this synthesis depends on a polycondensation reaction, it offers little control over polydispersity, average degree of polymerization, and primary structure sequence, all requirements for block-copolymer formation. Moreover, it is well documented that variation of the primary structure significantly influences the final optoelectronic properties.[3] Other strategies exist that permit nonaqueous processing;[4] for example, PPV can be obtained by ring-opening metathesis polymerization (ROMP) of functionalized bicyclo[2.2.2]octene.[5] In this case the living characteristics of the polymerization reaction offer primary structure control, but the final conversion to PPV requires forcing conditions (T = 265 or 200 °C in the presence of base catalyst).

We report herein a PPV synthesis by ROMP reaction of paracyclophene derivatives combining a living polymerization system with mild conversion of precursor polymer. These studies were prompted by the successful living and stereoregular ROMP of the model compound paracyclophan-1-ene.[6] The synthesis of the monomer, 9-[(*tert*-butyldimethylsilyl)oxy][2.2]paracyclophan-1-ene (**1**), is shown in Scheme 1. The key step involves conversion of tetrabromoparacyclophane by treatment with KOCMe$_3$ in *tert*-butyl methyl ether (MTBE), via a cyclophyne intermediate,[7] to 9(10)-bromo[2.2]paracyclophan-9-en-1-one, which exists as a mixture of isomers. Reduction of the carbonyl group by DIBAL in CH$_2$Cl$_2$ and protection of the resulting alcohol using *tert*-butyldimethylsilyl triflate generate 1(2)-bromo-9-[(*tert*-butyldimethylsilyl)oxy][2.2]paracyclophan-1-ene. Debromination with *n*-butyllithium provides **1** in 25% overall yield. All reactions in Scheme 1 are amenable to scale-up starting from 50 g of the tetrabromide.

Scheme 1



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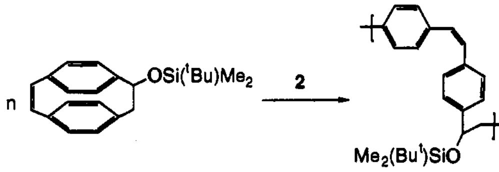
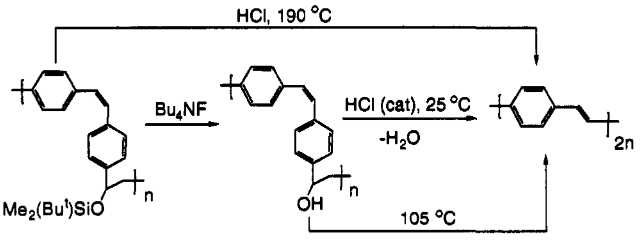
Polymerization of **1** proceeds in a living fashion using the Schrock initiator Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2,6-diisopropylphenyl) (**2**).[8] This process is identical to the living polymerization of paracyclophan-1-ene which has been described in detail elsewhere.[6] The silyl ether, located opposite the reactive olefin on the rigid cyclophane framework, does not interfere with propagation. Poly-**1** is produced with a narrow polydispersity and a molecular weight which increases linearly with the amount of monomer reacted. The reaction occurs in *cis*-specific fashion (~98%) and with approximately equal frequency of head-to-tail and head-to-head linkages. Unlike poly(paracyclophan-1-ene), poly-**1** containing a large portion of *trans* olefins (produced by either photolysis or I$_2$ catalysis) is soluble in common organic solvents, an important feature for processability.



1 *cis*-poly-**1**

Films of poly-**1** are stable up to ~400 °C (determined by TGA) but can be converted to *trans*-PPV at 190 °C under a flow of HCl(g) and N$_2$. The conversion is evidenced by UV spectroscopy (λ_{max} = 424 nm, Figure 1c)[9] and the appearance of a strong absorption in the IR spectrum at 963 cm^{-1} (due to *trans*-C–H, there are no bands observed near 880 cm^{-1} attributable to *cis*-C–H). Alternatively, desilylation of poly-**1** with Bu$_4$NF in THF generates poly(9-hydroxyl[2.2]paracyclophan-1–ene) (poly-**3**) quantitatively. Films of poly-**3** are stable up to 105 °C, where an 8% mass loss can be measured (by TGA) consistent with the loss of one molecule of water per unit monomer. Addition of a catalytic amount of HCl(g) permits dehydration at 25 °C.



poly-**1** poly-**3** PPV

The living polymerization of **1** together with the mild dehydration condition required by poly-**3** provides the opportunity to manufacture macromolecular structures containing PPV segments covalently linked to a second fragment chosen to tailor bulk properties. It is possible to enhance solubility using poly-NBE blocks (NBE = norbornene) with negligible interference in the photochemical processes of interest. In this way, PPV$_{30}$-*block*-

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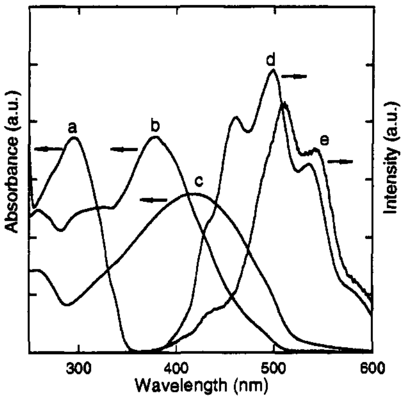

Figure 1. (a, b) Change in the optical absorption of poly-3_{15}-*block*-poly-NBE$_{200}$ in CH_2Cl_2 when treated with HCl(g) for a period of 6 h at 24 °C. (c) Absorption spectrum of PPV obtained from poly-1_{100}. (d) Photoluminescence spectrum of a solution of PPV$_{30}$-*block*-poly-NBE$_{200}$ in CH_2Cl_2. (e) Photoluminescence spectrum of a film of PPV$_{30}$-*block*-poly-NBE$_{200}$.

poly-NBE$_{150}$, produced from poly-3_{15}-*block*-poly-NBE$_{150}$,[10] is soluble in CH_2Cl_2 and permits the study of PPV formation and properties in solution. For example, the progression of the stilbene-like optical absorbance of poly-3_{15}-*block*-poly-NBE$_{150}$ (Figure 1a) to longer wavelengths (Figure 1b) upon addition of HCl is a clear manifestation of the increased delocalization and corresponding smaller π–π^* energy gap. Comparison of parts a–c of Figure 1 identifies the spectroscopy of these PPV oligomers as intermediate between the discrete molecular spectra observed in stilbene derivatives[11] and that which characterizes the broad distribution of conjugated chains in higher molecular weight PPV.

The photoluminescence spectrum of PPV$_{30}$-*block*-poly-NBE$_{150}$ is shown in Figure 1d while that of a film *cast from the same solution* is shown in Figure 1e. It is evident, from a comparison of the data, that a substantial quenching of lower wavelength emissions occurs in the solid state. It is reasonable to assume that in both instances photolysis results in the excitation of PPV chains of different lengths. In solution, the interaction between chains is minimized, and both high-energy emission (characteristic of shorter chains) and longer wavelength emission from longer chains can be observed. In the solid state, the close proximity between chains permits exciton migration to lower energy portions of the sample, which therefore become the predominant emitting species.[12]

In summary, a novel precursor approach to PPV is described. Preliminary studies show that PPV films are generated under mild conditions and that soluble PPV-containing block copolymers are accessible. This unique combination of features will provide a versatile method to tailor final bulk properties. Studies probing the contrast in photophysical properties between the solution and solid states are currently underway.

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Supplementary Material Available: Experimental procedures for the synthesis and polymerization of **1** and data for functionalized polymers (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(9) These results are unoptimized. PPV obtained via the sulfonium route can exhibit a considerably red-shifted λ_{max} using a precursor polymer of larger molecular weight and preordered chains. We are in the process of increasing the molecular weight of poly-**1** and optimizing other conditions in order to increase the extent of conjugation. See: (a) Stenger-Smith, J. D.; Lenz, R. W.; Wegner, G. *Polymer* **1989**, *30*, 1049. (b) Burn, P. L.; Bradley, D. D. C.; Friend, R. H.; Halliday, D. A.; Holmes, A. B.; Jackson, R. W.; Kraft, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3225. (c) Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Jackson, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 10117–10124 and references therein.

(10) Conveniently prepared by addition of 150 equiv of NBE to living poly-1_{15}. See ref 6 for a detailed discussion of conditions that lead to block copolymerizations of monomers such as **1**.

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