Synthesis of Organic and Water Soluble Poly(1,4-phenylenevinylenes) Containing Carboxyl Groups: Living Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboxybarrelenes

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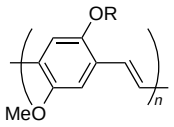
ABSTRACT: 2,3-Dicarboxybicyclo[2.2.2]octa-2,5,7-triene (barrelene) monomers (**4a,b**) were synthesized by a novel route and then polymerized by ring-opening metathesis polymerization (ROMP). Complete initiation of the ROMP initiator (**5**) and living polymerization of monomer **4b** were achieved by tuning the activity of **5** with hexafluoro-*tert*-butanol (HFB) and tetrahydrofuran (THF). The precursor polymers (**6a,b**) were readily converted to diester-substituted poly(1,4-phenylenevinylenes) (PPVs) (**7a,b**) by aromatizing the cyclohexadiene rings using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The resulting PPVs were highly luminescent, and polymer **7b**, bearing *tert*-butyl groups on its esters, was soluble in methylene chloride and chloroform. We found that partially oxidizing **6b** so that only 80% of the polymer units are aromatized increases both the solubility and photoluminescence quantum yield of **7b**. Deprotection of polymer **7b** by acid-catalyzed thermolysis of the *tert*-butyl groups followed by treatment with aqueous base produced a dicarboxylate PPV (**9**) that is soluble in water. Photoluminescence and UV/visible absorbance measurements show that, in solution, the PPVs synthesized are highly luminescent and blue shifted relative to films of unsubstituted PPV.

Introduction

Since the discovery that conjugated polymers can be used as the emissive layer in light-emitting diodes (LEDs),[1] extensive work has been done to investigate the physics and chemistry of these materials. One of the most common polymers used for these studies has been MEH−PPV and other dialkoxy-substituted poly-



R = 2-ethylhexyl

MEH–PPV

(1,4-phenylenevinylenes) (PPVs).[2−9] Unlike most conjugated polymers such as PPV and polyparaphenylene (PPP), MEH−PPV has the advantage of being soluble in common organic solvents, so devices can be easily fabricated by spin casting the emissive layer onto the LED anode. In addition, the positions of the HOMO and LUMO of MEH−PPV closely match the electron affinity and ionization potentials of indium tin oxide (ITO) and calcium—a commonly employed anode and cathode respectively—so devices made using these electrodes have high efficiencies.[6] Using MEH−PPV has yielded extensive progress in the study of device fabrication and optimization of both single-layer and multilayer LEDs,[6,7] and more recently this material has been used as the emissive layer in some of the first organic polymer lasers.[5,8]

One potential drawback of using MEH−PPV in electroluminescent (EL) devices, however, is that the electron-donating groups on the polymer destabilize its HOMO and LUMO[10] so that the polymer is more readily oxidized by oxygen than unsubstituted PPV. Because of this instability, devices made with MEH−PPV require rigorous encapsulation to prevent oxidation of the emissive layer.[7,11,12] Oxidation of the polymer may remain a problem even with encapsulation, however, since recent studies show that ITO may be a source of oxygen.[13] In contrast to the effect of electron-donating alkoxy groups, electron-withdrawing groups stabilize PPV's HOMO and LUMO levels, making it less susceptible to oxidation. Electron-withdrawing groups also increase the electron affinity of PPV, thus making it easier to inject electrons into the polymer. This increased electron affinity allows the use of electrodes with higher work functions than that of calcium, such as aluminum, which is more air stable than calcium. In addition, this heightened electron affinity can improve device efficiency by yielding a better balance between electrons and holes in the polymer. While PPV is a good hole conductor and a poor electron conductor, electron-accepting substituents improve PPV's electron injection and electron transport properties and, therefore, improve device efficiency by increasing the number of holes that pair with electrons, thereby reducing the number of holes that are quenched at the negative electrode.[12]

While electron-withdrawing groups can improve the properties of PPV for EL applications for the variety of reasons mentioned above, only a few PPVs containing electron-withdrawing groups have been synthesized.[12,14−17] The majority of these polymers have been soluble only in their unconjugated, precursor form, and, therefore, are not ideal for LED applications, since it is desirable to be able to spin cast the conjugated polymer. Of the polymers synthesized, several have shown a blue shift in their absorbtion and emission spectra, which contrasts with the red shift predicted for conjugated polymers bearing electron-accepting groups.[10] It is, therefore, desirable to synthesize new, soluble PPVs containing electron-withdrawing groups not only for the advantages these polymers will have for LED applications but also to examine how the emission wavelength of the polymers shifts with different electron-withdrawing substituents.

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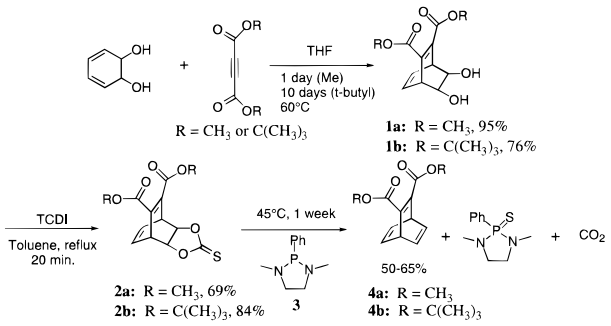
Scheme 1



In the past, ring-opening metathesis polymerization (ROMP) has been used to synthesize several conjugated and electroluminescent polymers. Edwards and Feast reported the first synthesis of a conjugated polymer by ROMP with their precursor route to polyacetylene (PA).[18,19] Their synthesis was soon followed by our direct routes to unsubstituted PA and soluble, substituted PAs from readily available cyclooctatetraene monomers.[20−22] We later reported the synthesis of unsubstituted PPV[23] and several soluble, substituted PNV homopolymers and well defined block copolymers.[24,25] We herein report the synthesis of soluble PPVs containing electron-withdrawing ester substituents by a mild ROMP precursor route. While carbonyl defects in the polymer backbone have been proposed to quench PPV's luminescence,[26] the conjugated polymers we obtained with carbonyls present as pendant groups have high photoluminescence quantum yields.

To accomplish the synthesis of PPVs by ROMP, we first synthesized barrelene monomers, which can be polymerized to produce a precursor to PPV. While the syntheses of dibenzobarrelene[27−30] and substituted and unsubstituted benzobarrelenes[31,32] were previously reported in high yields and in large quantities, the synthesis of barrelenes has historically been complicated.[33]

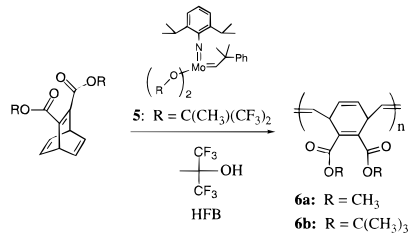
barrelene benzobarrelene

In general, the available syntheses of barrelene have low overall yields and require difficult separations because most acetylenes are not sufficiently activated to undergo an efficient Diels−Alder reaction with benzene.[34−36] To overcome the lack of reactivity of most dieneophiles with benzene, we have used *cis*-3,5-cyclohexadiene-1,2-diol as a benzene equivalent in the Diels−Alder reaction (see Scheme 1). This molecule, which we have previously used in a protected form for the synthesis of alkylated benzobarrelenes,[24,32] affords a facile reaction with diester-substituted acetylenes to produce a Diels−Alder adduct that is readily converted to barrelenes. The overall synthesis yields multigram quantities of the desired monomers and allows purification by standard techniques. From these barrelene monomers, we have synthesized dicarboxy-substituted PPVs which are soluble in organic solvents and water.

Results and Discussion

Monomer Synthesis. The barrelene monomers required for the synthesis of PPV by ROMP were obtained as shown in Scheme 1. Diels−Alder reaction of the appropriate acetylene with the benzene equivalent *cis*-3,4-cyclohexadiene-1,2-diol produced the bicyclic diol in high yield. As previously observed, dimethyl acetylenedicarboxylate was found to be significantly more reactive than di-*tert*-butyl acetylenedicarboxylate.[37] The reduced yield for **1b** results from the fact that some of the di-*tert*-butyl acetylenedicarboxylate eventually decomposed to the acid, which then catalyzed the decomposition of the diol starting material to phenol, thus producing a reduced yield of the Diels−Alder adduct. Decomposition of the *cis*-3,5-cyclohexadiene-1,2-diol can be prevented by addition of calcium carbonate, which neutralizes any acid formed by thermolysis of the acetylene esters.

Scheme 2



From the diols **1a,b** the corresponding barrelenes **4a,b** were obtained in two steps by first forming the thiocarbonates **2a,b** by reaction of **1a,b** with thiocarbonyldiimidazole (TCDI).[38] The thiocarbonate moiety was then eliminated through a carbene intermediate to yield the final products **4a,b**. For both the methyl and *tert*-butyl esters, the Diels−Alder reaction yielded both syn and anti isomers of **1a,b**. NOE experiments and comparison to previously reported compounds[39,40] show that the major product is the anti isomer. When converting **2a,b** to **4a,b**, the anti isomer reacted much faster with its conversion complete after 3 days, while complete conversion of the syn isomer took up to 12 days under the same conditions. The reason for the use of **3** rather than trialkyl phosphites was that **3** accomplishes the same conversion at a much lower temperature,[41] which is important to minimize retro Diels−Alder decomposition of the thiocarbonate starting materials and barrelene products.

Unlike the previously reported synthesis of barrelene,[36] products of all steps of the syntheses presented here were readily purified by standard techniques such as column chromatography or recrystallization. The ease of synthesis and purification has allowed the production of barrelene monomers in the large quantities desired for characterization of the polymers and study of the optical and electronic properties of these materials.

Polymer Synthesis. As shown in Scheme 2, ROMP of **4a,b** was accomplished using a molybdenum metathesis initiator (**5**) in the presence of hexafluoro-*tert*-butanol (HFB). The next section discusses how the addition of this alcohol and THF tunes the activity of **5**. Using the HFB-activated polymerization system, it was observed that polymerization of **4b** was much faster than that of **4a**, with **4b** being completely consumed after 3 h, but with the polymerization of **4a** reaching only 80−90% completion after 1 week.

The slower reaction of **4a** is most likely due to coordination of the polymer chain to the catalyst, as shown in Figure 1. Such coordination is expected to deactivate the molybdenum carbene and thereby reduce the rate of monomer consumption, for both electronic and steric reasons. Alternatively, the monomer could coordinate to the catalyst. Monomer coordination would not have the favorable chelate effect but would similarly deactivate the molybdenum initiator. For monomer **4b**

Table 1. Data for Polymerization of 4a and 4b in the Presence of HFB and THF

sample	monomer	[M]/[**5**]	equiv HFB	equiv THF	$\bar{M}_n$	PDI	% initiation[a]
1	**4a**	45	15	0	16 681	1.44	
2	**4b**	45	0	0	34 676	1.15	77.3%
3	**4b**	45	15	0	19 587	1.22	85.9%
4	**4b**	45	15	10	21 236	1.11	91.6%
5	**4b**	45	15	25	17 754	1.11	100%
6	**4b**	99	15	0	39 318	1.15	100%

[a] Determined by the ratio of initiated **5** to total **5** as determined by integration of the carbene region (≈14−10 ppm) of the ^{1}H NMR spectrum.

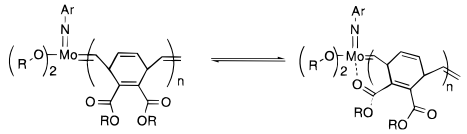


Figure 1. Coordination of the growing polymer chain to the molybdenum initiator.

the polymerization reaction is much faster, and propagating carbene protons can be observed throughout the reaction. This indicates that coordination of the monomer or growing polymer to molybdenum is weaker than that for **4a** due to the steric interaction between the *tert*-butyl groups and the molybdenum and, therefore, that deactivation of **5** is diminished. Several different propagating species are observed during the polymerization of **4b**, and propagating carbene is not observed during the polymerization of **4a**; additional study will be required to determine the exact nature of the intermediate carbene species during the course of these reactions.

^{1}H and ^{13}C NMR of **6a,b** show that both cis and trans vinylene units are formed between the cyclohexadiene rings during the polymerization and that polymer **6b** has a higher percentage of cis linkages than polymer **6a**.[42,43] While cis units can shorten the conjugation length of the final PPV, since they cause a twist in the polymer chain, they have also been found to have the advantage of improving the solubility of conjugated polymers[24] and increasing the polymers' quantum yield.[44] For electroluminescence applications, improved solubility eases preparation of polymer thin films by making it easier to spin cast the polymers, and increased quantum yield improves device efficiency.

Catalyst Activation. While **5** alone can polymerize the monomers, it was found that the addition of HFB increased the rate of reaction—the reaction requires 36 h to reach completion with 5 alone but is complete after 3 h with 15 equiv of HFB—and resulted in more of **5** being initiated, as observed by ^{1}H NMR. While the improvement in initiation was less pronounced than that previously observed for the polymerization of benzobarrelenes,[25] the addition of alcohol offered some improvement in the initiation of **5** and greatly reduced the reaction time. As shown in entry 6 of Table 1, complete initiation of **5** can be achieved using this polymerization system by increasing the monomer to initiator ratio.

Complete initiation can also be accomplished at lower monomer to initiator ratios by adding THF to the reaction mixture. Addition of this Lewis base, which coordinates to the molybdenum the same way that the monomer is proposed to in the above section, allowed full initiation of **5** because it slowed propagation more than initiation. We have previously used trimethyl phosphite to achieve complete initiation of a tungsten initiator for the polymerization of cyclobutene and norbornene monomers,[45,46] but we found that the less coordinating THF was sufficient for complete initiation of **5** by **4b**. Achieving full initiation was desirable to obtain a well controlled polymerization and to show that it will be possible to obtain well defined block copolymers. As shown in Table 1, while the addition of HFB does not improve the polymer's PDI, the presence of THF not only produces full initiation at low monomer to initiator ratios but also yields polymers with lower polydispersities than those of the polymers produced using **5** alone, because it reduces the rate of propagation relative to the rate of initiation.

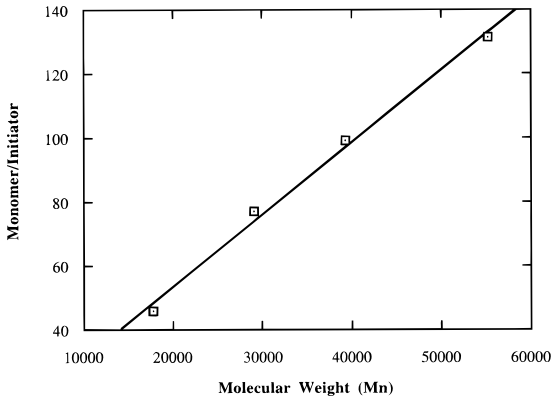


Figure 2. Monomer/initiator ratio vs number average molecular weight.

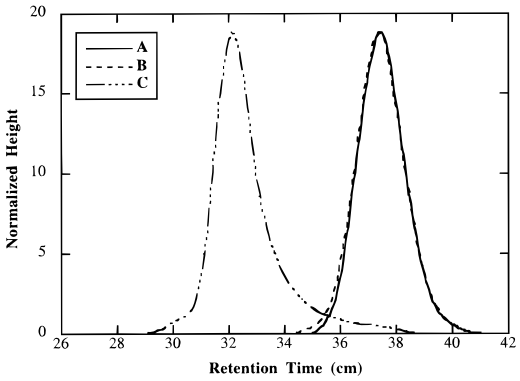
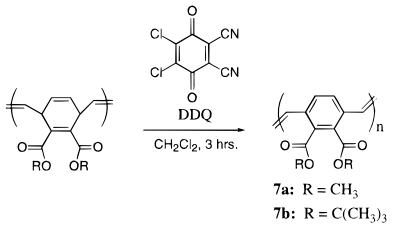


Figure 3. Test for chain transfer, chain termination, and backbiting.

"Livingness" Studies. To determine whether the polymerization of **4b** using the HFB-activated polymerization system was living, several tests were done to check for chain termination, chain transfer, chain-coupling, and backbiting reactions.[47−49] The first such test was done by polymerizing different amounts of monomer **4b** with the same amount of initiator **5**. Results of this experiment, displayed in Figure 2, show that the molecular weight of the polymer increases linearly with the monomer to initiator ratio, as is expected for a living polymerization.

The second test, whose results are shown in Figure 3, was done by first polymerizing one batch of monomer, with a monomer to initiator ratio of 50, to completion. After the reaction was complete, the reaction mixture was divided into three equal amounts. One of the

Scheme 3



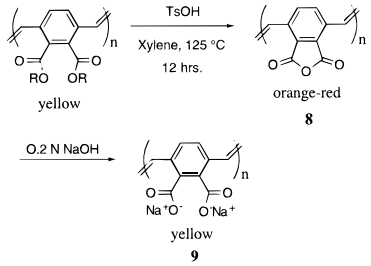
aliquots, **A**, was immediately quenched with benzaldehyde, which deactivates the initiator, to establish a reference point for molecular weight and polydispersity. The second aliquot, **B**, was saved to determine whether backbiting or chain-coupling reactions, which would cause an increase in the polydispersity, occur over time. Additional monomer (250 equiv) was added to the third aliquot, **C**, to continue the polymerization. This sample was used to determine if chain termination occurred before the second batch of monomer was added. Following completion of the polymerization in aliquot **C**, it and aliquot **B** were both quenched with benzaldehyde. As shown in the graph, aliquot **C** shows that little if any chain termination occurred before the second batch of monomer was added. While the tailing of this peak indicates that some chain termination may be occurring as the polymer chains become longer, the fraction of terminated chains is quite small. In addition, the observed molecular weight increase is comparable to that expected using the data in Figure 2 as a calibration curve. Comparison of aliquots **A** and **B** shows that there was no broadening of the polymer's molecular weight distribution and no increase in molecular weight over time. This result indicates that the initiator at the end of the polymer chain is not backbiting into the chain that it is connected to or into other polymer chains and that coupling reactions or other polymer degradation reactions do not occur in the presence of unquenched initiator.

The results of these two experiments present strong evidence that the reaction is living and that this system is well suited to the synthesis of block copolymers.

Polymer Purification and Aromatization. As described in the above section, completed polymerizations were terminated by adding a few drops of benzaldehyde to the reaction mixture.[50] Following this procedure, polymers **6a,b** were purified by pipetting the reaction solution into degassed methanol (degassed solvents were used to prevent oxidation of the polymers by oxygen). The white polymer precipitate was isolated by centrifuging this mixture and then decanting the green-brown solvent under argon. To further purify the polymers, they were redissolved in either degassed methylene chloride or benzene and then reprecipitated using degassed methanol. The mixture was again centrifuged and the solvent decanted. This process was repeated until the decanted solvent mixture was colorless. The polymers were then dried under vacuum to yield a brittle, light-brown solid in the case of **6a** and a brittle, light-yellow solid for **6b**.

Aromatization of the precursor polymers **6a,b** was achieved using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as shown in Scheme 3.[51] This reaction occurs slowly over 3−5 h at room temperature in methylene chloride to yield a bright-yellow, cloudy mixture in the case of **7b** and a cloudy orange mixture for **7a**. For **7b** it was sometimes desirable to have the polymer be only partially aromatized, since the partially converted polymer is much more soluble, and therefore better for spin-casting films, and also has a higher photoluminescence

Scheme 4



quantum yield. Partial aromatization of the polymer was accomplished by simply adding <1 equiv of the DDQ oxidant. In all cases, the polymers were purified by repeated precipitation, as described above for **6a,b**. For the conjugated polymers, either methylene chloride or chloroform was used to dissolve or suspend (**7a** had low solubility in all solvents) the polymers, and reprecipitation was then accomplished using methanol as before.

The aromatized polymers **7a,b** were either bright yellow or orange and luminesced strongly in the yellow-green part of the visible spectrum under a hand-held UV lamp. Both polymers are soluble at low concentrations in methylene chloride and chloroform with **7b** being the more soluble of the two polymers. The solubility of **7b** was further improved when the polymer was only partially aromatized. When the polymer contains 80% aromatized units, it is soluble in concentrations of 40 mg/mL in methylene chloride.

While ^1H and ^{13}C NMR of **6a,b** show peaks indicative of *cis*- and *trans*-vinylene units, NMR of **7b** shows only one type of polymer, indicating that most of the cis units formed during polymerization isomerize to the trans polymer during oxidation. Upon complete aromatization, all signals of **6b** not associated with the *tert*-butyl groups are shifted to the aromatic region of the ^1H NMR spectrum. Two signals are observed in the region from 8 to 7 ppm, corresponding to the protons on the benzene rings and those on the adjacent conjugated olefins. Similarly, ^{13}C NMR shows that what had been the bridgehead carbons on **4b** are now shifted into the aromatic region. Infrared spectra of the polymers confirm that trans olefin linkages are present in **7a,b** with a signal at 957 cm^{-1}.

Deprotection of 7b. Polymer **7b** was converted to the water soluble dicarboxylate PPV **9**, as shown in Scheme 4. Conversion to the anhydride[52,53] occurs rapidly in refluxing xylene in the presence of a small amount of acid catalyst. The bright-red anhydride formed (**8**) is insoluble in all organic solvents and water but can be identified by its two strong carbonyl stretches in the infrared spectrum at 1839 and 1763 cm^{-1}. Upon conversion to **9**, which is readily accomplished by mixing **8** with aqueous base, the polymer dissolves and resumes the bright-yellow color of **7b**. Polymer **9** is soluble in aqueous base, and uniform, luminescent films of this polymer can be formed by spin casting the polymer from aqueous solution.

Thermogravimetric analysis of **7b** under argon reveals that the same conversion to the anhydride occurs at 237 °C in the absence of acid catalyst. Further decomposition begins around 512 °C and continues until all of the polymer is gone at 700 °C. The anhydride **8** loses very little mass until 506 °C and then undergoes the same course of decomposition observed for **7b**.

Spectroscopic Study of PPVs. The photoluminescence spectra, shown in Figure 4, and absorbance data in Table 2, both of which were obtained on solutions of

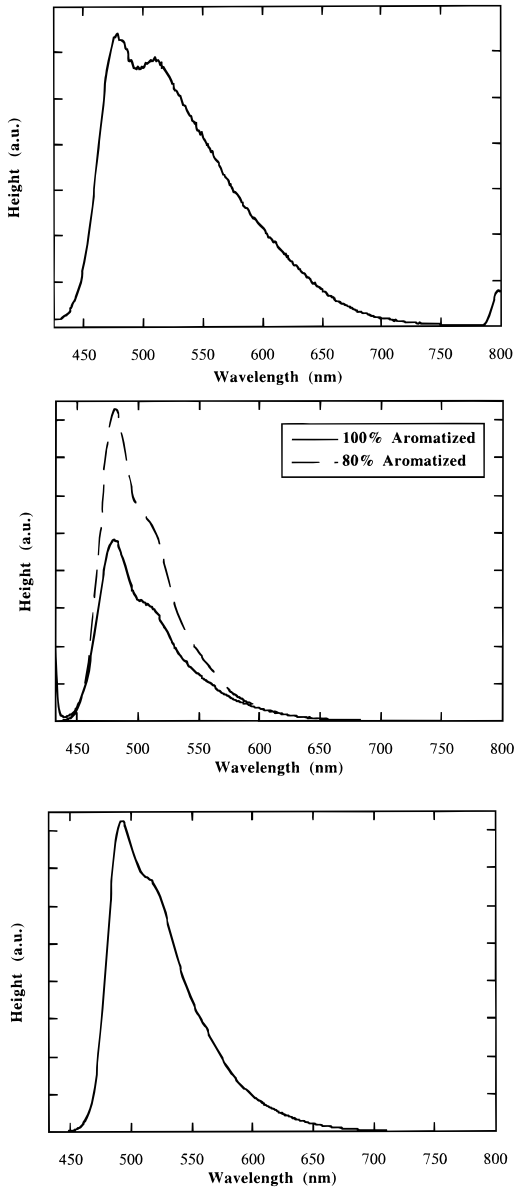


Figure 4. (a, top) Photoluminescence of polymer **7a**. (b, middle) Photoluminescence of polymer **7b** containing 80% and 100% aromatized units. (c, bottom) Photoluminescence of polymer **9**.

the polymers, show that the absorbance and emission maxima of **7a,b** and **9** are strongly blue shifted relative to those of films of unsubstituted PPV. While electronic arguements have been invoked for blue shifts in other PPVs bearing electron-withdrawing groups,[14,15,17] the shift observed for **7a,b** and **9** is probably at least partially a result of a twist in the polymer backbone due to steric interaction of the carboxyl groups and solution-induced disorder.

As mentioned earlier, samples of **7b** were studied at 80% and 100% aromatization. In addition to offering better solubility, the partially aromatized polymer shows a higher quantum yield than the fully conjugated version (see Figure 4b). A similar quantum yield improvement has been observed for other conjugated polymers containing saturated units and was previously proposed to result from the unconjugated units acting as insulating segments which inhibit the movement of excitons and thereby reduce migration to quenching sites.[2]

It is also important to note that polymers **7a,b** and **9**, which each bear two carboxyl groups, are highly luminescent—polymer **7b** containing 80% aromatized units has a quantum yield of approximately unity while polymer **9** has a quantum yield of 10−20%. In contrast, the PPV anhydride **8**, whose carbonyl groups are forced into the PPV plane and therefore are in conjugation with the rest of the polymer, appears to be much less luminescent than either **7a,b** or **9**. So while it has been proposed that carbonyl defects in the polymer backbone quench PPV's luminescence,[26] the carbonyls present as pendant groups on **7a,b** and **9** do not quench the luminescence of these polymers.

Table 2. Absorbance and Photoluminescence Data for Polymers 7a,b and 9

polymer[a]	solvent	λ_{abs}(max)	λ_{em}(max)[b]
PPV[c]		442	558
7a	$CHCl_3$	400	489
7b (80%)	$CHCl_3$	410	489
7b	$CHCl_3$	408	489
9	0.1 N NaOH (aq)	424	501

[a] Samples were fully aromatized except as noted in parentheses. [b] Corrected so that a $Ru(bpy)_3Cl_2$ standard was at 628 nm.[55] [c] See refs 14, 57, and 58.

Conclusions

The results presented in this paper show that PPVs bearing electron-withdrawing groups are readily accessible through a ROMP presursor route starting from barrelene monomers. To prepare the desired polymers, we first developed an efficient synthesis of substituted barrelenes—a previously elusive class of compounds. Our new route to these molecules allows them to be made not only in good yields but also in the large quantities required for studying their ROMP polymers. The extension of this route to include other barrelene derivatives is currently under investigation.

We also showed that the ROMP initiator **5** used in these studies can be tuned using HFB and THF to yield a living polymerization system for barrelenes. Use of this system allowed the synthesis of homopolymers and a diblock homopolymer with low polydispersity. Examining different monomers has shown that the alkyl group on the diester barrelenes strongly affects the rate of polymerization by determining how strongly the monomer or polymer chain can coordinate to the molybdenum initiator.

Chemical aromatization of the ROMP precusor polymers to yield soluble PPVs was readily achieved in solution at room temperature. Incomplete aromatization of the precursor polymers increased both the solubility and photoluminescence quantum yield of the resulting PPVs. In addition to the organic soluble polymers, we also prepared a dicarboxylate PPV **9**, which is soluble in aqueous base, by removing the *tert*-butyl groups from **7b** through acid-catalyzed thermal elimination.

Polymers **7a,b** and **9** were all highly luminescent, showing that their high concentration of pendant carbonyl groups do not act as efficient quenching sites. The absorbance and emission maxima of solutions of the polymers showed a strong blue shift relative to those of films of unsubstituted PPV. This shift is most likely due to a reduction in the polymers' conjugation length resulting from a twist in the polymer backbone caused by steric interaction of the carboxyl groups and by solution-induced disorder. Films of these materials and other PPVs bearing electron-withdrawing groups are currently being studied to determine the origin and magnitude of the shifts observed.

Experimental Section

General Methods and Materials. NMR spectra were recorded on a QE Plus 300 MHz (300.1 MHz, ^{1}H; 75.33 MHz, ^{13}C) spectrometer. Infrared spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. Elemental analyses were performed by Caltech Analytical Labs or Mid-West Microlab. High-resolution mass spectra were obtained from UC Riverside Mass Spectrometry Facility. UV/visible spectra were recorded on a HP Vectra ES/12 spectrometer. Thermogravimetric analyses were carried out using a TGA 7 Thermogravimetric Analyzer. Gel permeation chromatography (GPC) utilized an AM Gel Linear 10 column and a Knauer differential refractometer. Methylene chloride (Burdick and Jackson HPLC grade) was used as the eluent for all GPC measurements. Molecular weights are uncorrected and reported as compared to Shodex polystyrene standards with molecular weights ranging from 2.95×10^3 to 2.40×10^6. Emission spectra were recorded on an SLM 8000 C Spectrofluorimeter. THF was dried by passing through activated alumina columns. *cis*-3,5-Cyclohexadiene-1,2-diol was obtained from ICI. Xylene was purchased from Aldrich in a Sure Seal container. Thiocarbonyldiimidazole (TCDI), 1,3-dimethyl-2-phenyl-1,3-diaza-2-phospholidine (**3**) and DDQ were purchased from Aldrich and used without further purification. Methanol, dichloromethane, and chloroform were degassed by purging with dry argon for a minimum of 30 min. Initiator **5** was prepared as previously reported.[54]

Photoluminescence Measurements. All measurements were performed on solutions that were diluted so that the emission maximum was on scale with a $Ru(bpy)_3Cl_2$ standard that was approximately 1×10^{-5} M. The exact concentration used in calculating quantum yields (7.6×10^{-6} M) was calculated from the absorbance of this solution at 453 nm and the reported extinction coefficient.[55] Solutions used for **7a**, **7b**, and **9** were 1.47×10^{-6}, 1.06×10^{-7}, and 2.23×10^{-7} M, respectively. All polymer solutions were prepared using degassed solvent. Quantum yields for the polymers were calculated by comparison to a $Ru(bpy)_3Cl_2$ standard using the equation

$$\Phi_{poly} = \frac{I_{poly} \cdot \epsilon_{Ru} c_{Ru}}{I_{Ru} \cdot \epsilon_{poly} c_{poly}} \cdot \Phi_{Ru}$$

Integration values, *I*, were measured on spectra that had been corrected for detector response using the software provided with the SLM 8000 C Spectrofluorimeter. A value of 0.028 ± 0.002 was used for Φ_{Ru}.[56] The $Ru(bpy)_3Cl_2$ solution was equilibrated with air.

Dimethyl 2,3-Dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate (1a). Under air, a 50 mL round bottom flask (RBF) was charged with 9 mL of dimethyl acetylenedicarboxylate (73.2 mmol) and 4.01 g (35.7 mmol) of *cis*-3,5-cyclohexadiene-1,2-diol. The solution was heated at 60 °C for 1 day. Excess acetylene was removed under vacuum to yield a viscous yellow oil. The oil was loaded onto a column containing 1000 mL of silica gel and was eluted with 1000 mL of 50% ethyl acetate/hexane followed by 1000 mL of 80% ethyl acetate/hexane and 1000 mL 90% ethyl acetate/hexane to yield two product isomers separately. Both isomers were light-yellow oils initially, but the anti isomer became a waxy solid upon standing. Total yield of both isomers was 95% (8.61 g, 33.9 mmol). ^{1}H NMR ($CDCl_3$): anti isomer, δ 6.47 (m, 2H), 4.21 (m, 2H), 3.89 (m, 2H), 3.78 (s, 6H), 2.64 (m, 2H, OH); syn isomer, δ 6.28 (m, 2H), 4.20 (m, 2H), 3.81 (s, 6H), 3.78 (m, 2H), 3.25 (m, 2H). ^{13}C NMR ($CDCl_3$) anti, δ 165.73, 140.01, 131.29, 66.46, 52.27, 46.14; syn, δ 166.55, 139.45, 131.65, 65.87, 52.18, 45.86. FTIR: anti, 3430, 3001, 2955, 2848, 1716, 1646, 1604, 1437, 1401, 1356, 1280, 1223, 1168, 1147, 1093, 1061, 979, 881, 827, 803, 792, 775 cm^{-1}. HRMS: calcd for $C_{12}H_{15}O_6H$ $(MH)^+$, 255.0865; found, 255.0871. Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.14; H, 5.81.

Reaction of 1a with 2,2-Dimethoxypropane. Each isomer of **1a** (55 mg, 0.22 mmol) was loaded into a separate 10 mL RBF, and 0.3 mL (254 mg, 2.4 mmol) of 2,2-dimethoxypropane was added. A few grains of *p*-toluenesulfonic acid was added to each flask. After stirring for 40 min, excess 2,2-dimethoxypropane was removed under vacuum. ^{1}H NMR of the acetals showed the product of protection of the major isomer of **1a** to be the previously reported anti acetal.[40] ^{1}H NMR ($CDCl_3$): anti, δ 6.38 (m, 2H), 4.38 (m, 2H), 4.22 (m, 2H), 3.78 (s, 6H), 1.34 (s, 3H), 1.26 (s, 3H); syn, δ 6.33 (m, 2H), 4.30 (m, 2H), 4.26 (m, 2H), 3.80 (s, 6H), 1.35 (s, 3H), 1.27 (s, 3H).

Di-*tert*-butyl 2,3-Dihydroxy-5,7-bicyclooctadiene-5,6-dicarboxylate (1b). Acid impurities were removed from the di-*tert*-butyl acetylenedicarboxylate by loading it onto a plug of silica gel and eluting with 10% ethyl acetate/hexane. After removal of solvent, 3.8 g (16.8 mmol) of this purified material was put in a 50 mL RBF along with 0.924 g (8.24 mmol) of *cis*-3,5-cyclohexadiene-1,2-diol. The flask was purged with argon, and then 2 mL of dry THF was added. The reaction was heated for 10 days at 60 °C, after which time ^{1}H NMR showed no diol starting material. Upon heating, the acetylene melted, and the diol dissolved. As the reaction progressed, the solution became cloudy, and when the reaction was complete a significant amount of product had precipitated as a yellow solid. Once the reaction was complete, the reaction mixture was dissolved in ethyl acetate and 25 g of silica gel was added. Solvent was evaporated to yield a free-flowing solid, which was then loaded onto a plug of 100 mL of silica gel and eluted with 50% ethyl acetate/hexane. Following removal of solvent, 2.12 g (6.302 mmol) of the pale-yellow solid product was obtained as a mixture of two isomers. Yield = 75%. *Note*: To obtain a good yield, it is important that the temperature is not allowed to rise much above 60 °C. This reaction can also be done on a larger scale using 15 g of the diol starting material. Adding 3 equiv of calcium carbonate relative to acetylene to this reaction was found to prevent the formation of phenol. ^{1}H NMR ($CDCl_3$): anti, δ 6.44 (m, 2H), 4.11 (m, 2H), 3.87 (m, 2H), 2.64 (bs, 2H), 1.50 (s, 18H); syn, 6.25 (m, 2H), 4.11 (m, 2H), 3.71 (m, 2H), 2.64 (bs, 2H), 1.52 (s, 18H). ^{13}C NMR ($CDCl_3$): anti, δ 164.57, 139.89, 131.61, 82.49, 66.84, 46.60, 27.97; syn, 165.86, 139.05, 131.68, 82.09, 66.27, 46.09, 27.90. FTIR: anti, 3401, 3072, 2890, 2934, 1708, 1645, 1605, 1478, 1458, 1437, 1368, 1283, 1256, 1165, 1142, 1083, 1058, 979, 845 cm^{-1}. HRMS: calcd for $C_{18}H_{27}O_6$ $(MH)^+$, 339.1801; found, 339.1818. Anal. Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found: C, 63.79; H, 7.82.

Dimethyl 2,3-((Thiocarbonyl)dioxy-5,7-bicyclooctadiene-5,6-dicarboxylate (2a). Compound **1a** (2.38 g, 9.35 mmol) and 1.94 g (90% pure, 9.80 mmol) of thiocarbonyldiimidazole (TCDI) were loaded into a 50 mL flask and purged with argon. Dry toluene (30 mL) was added to yield a yellow solution containing undissolved TCDI. The solution was heated in an oil bath that was preheated to 120 °C for 30 min. After the solution was cooled to room temperature, it was poured into 25 mL of 1 M HCl. The aqueous layer was extracted with 4×50 mL of ether. The combined organic layers were then extracted with 2×5 mL of 1 M HCl and 10 mL of brine and then dried over magnesium sulfate. Evaporation of the solvent yielded 1.9 g of the product as a yellow solid. Yield = 69%. ^{1}H NMR ($CDCl_3$): anti, δ 6.54 (m, 2H), 5.00 (m, 2H), 4.57 (m, 2H), 3.82 (s, 6H); syn, δ 6.43 (m, 2H), 4.95 (m, 2H), 4.60 (m, 2H), 3.83 (s, 6H). ^{13}C NMR ($CDCl_3$): anti, δ 191.22, 164.25, 139.32, 131.14, 81.01, 52.70, 42.53; syn, δ 191.08, 164.64, 138.88, 132.18, 80.65, 52.73, 42.40. FTIR: anti, 3004, 2954, 2848, 1805, 1722, 1647, 1605, 1436, 1369, 1351, 1281, 1229, 1159, 1140, 1067, 996, 954, 914, 895, 820, 757, 737 cm^{-1}. HRMS: calcd for $C_{13}H_{12}O_6S$, 296.0352; found, 296.0350. Anal. Calcd for $C_{13}H_{12}O_6S$: C, 52.70; H, 4.08. Found: C, 53.39; H, 4.20.

Di-*tert*-butyl 2,3-((thiocarbonyl)oxy-5,7-bicyclooctadiene-5,6-dicarboxylate (2b). Compound **1b** (2.12 g, 6.30 mmol) and TCDI (1.31 g, 90% pure, 6.62 mmol) were loaded into a 100 mL flask, and the flask was purged with argon. Dry toluene (20 mL) was added to yield a yellow solution containing undissolved TCDI. The solution was heated in an oil bath that was preheated to 120 °C for 15 min. After the yellow solution was cooled to room temperature, it, which also contained a black precipitate, was poured onto a plug of 100 mL of silica gel and eluted with 50% ethyl acetate/hexane. Evaporation of the solvent yielded 2.15 g (5.65 mmol) of the product as a light-yellow solid. Yield = 90%. ^{1}H NMR ($CDCl_3$): anti, δ 6.49 (m, 2H), 4.98 (m, 2H), 4.45 (m, 2H), 1.50

(s, 18H); syn, δ 6.31 (m, 2H), 4.88 (m, 2H), 4.42 (m, 2H), 1.46 (s, 18H). ^{13}C NMR ($CDCl_3$): anti, δ 191.50, 163.08, 139.15, 131.27, 83.24, 81.36, 42.92, 27.97; syn, δ 191.10, 163.37, 138.44, 131.94, 82.40, 80.63, 42.43, 27.82. FTIR: anti, 2981, 2934, 1806, 1712, 1646, 1603, 1477, 1447, 1393, 1369, 1349, 1286, 1162, 1139, 1064, 1034, 995, 947, 893, 844, 821, 757, 710 cm^{-1}. HRMS: calcd for $C_{19}H_{24}O_6S$, 380.1288; found, 380.1283. Anal. Calcd for $C_{19}H_{24}O_6S$: C, 59.98; H, 6.36. Found: C, 59.82; H, 6.53.

Dimethyl Barrelene-2,3-dicarboxylate (4a). A 25 mL RBF was charged with 1.85 g (6.24 mmol) of **2a** and 3.6 mL (97% pure, 18.0 mmol) of **3** to yield a brown mixture with a lot of undissolved thiocarbonate. The mixture was heated under argon in an oil bath at 40 °C for 5 days. The brown solution was then loaded onto a silica gel column and eluted with methylene chloride. After evaporation of solvent, 0.814 g (3.70 mmol) of the product was obtained as a pale-yellow oil. Yield = 61%. ^{1}H NMR ($CDCl_3$): δ 6.87 (m, 4H), 5.11 (m, 2H), 3.77 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 165.79, 148.35, 139.39, 51.87, 49.00. FTIR 3075, 3003, 2954, 2845, 1714, 1648, 1602, 1580, 1435, 1331, 1313, 1270, 1236, 1192, 1118, 1056, 966, 939, 902, 885, 864, 844, 801, 751, 727 cm^{-1}. HRMS: calcd for $C_{12}H_{13}O_4$ $(MH)^+$, 221.0811; found, 221.0806. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 64.32; H, 5.72. (The sample contained ≈5% dimethyl benzene-1,2-dicarboxylate.)

Di-*tert*-butyl Barrelene-2,3-dicarboxylate (4b). A 100 mL RBF was charged with 13.57 g (35.66 mmol) of **2b** and 21 mL of **3** to yield a brown mixture with a lot of undissolved **2b**. The mixture was heated under argon in an oil bath at 40 °C for 1 week. The brown solution was then loaded onto a silica gel column and eluted with 10% ethyl acetate/hexane. After evaporation of solvent, the product was obtained as 6.7 g of a white crystalline solid containing ≈10% of the retro Diels−Alder benzene product. This mixture was dissolved in 200 mL of hot hexane and then cooled to −50 °C overnight. Solvent was decanted, and the solid was washed with −50 °C pentane. Drying the solid under vacuum yielded the product as a colorless to white crystalline solid, and removal of solvent from the mother liquor yielded the benzene decomposition product as a clear colorless liquid. To remove any acid formed while heating, the solid was eluted through a plug of silica gel with 10% ethyl acetate/hexane. Solvent was removed to yield 5.9 g (19.38 mmol) of the pure product as a white powder. Yield = 51%. ^{1}H NMR ($CDCl_3$): δ 6.84 (m, 4H), 5.02 (m, 2H), 1.49 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 164.84, 148.33, 139.65, 81.55, 49.57, 28.02. FTIR: 2974, 2936, 1728, 1695, 1647, 1601, 1581, 1472, 1452, 1392, 1365, 1337, 1315, 1273, 1158, 1123, 1108, 1051, 1021, 937, 901, 880, 845, 765, 742 cm^{-1}. HRMS: calcd for $C_{18}H_{24}O_4$, 304.1669; found, 304.1675. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.22; H, 7.95.

Poly(dimethyl barrelene-2,3-dicarboxylate) (6a). Inside a nitrogen-filled drybox, 0.423 g (1.92 mmol) of **4a** was dissolved in 4.37 g of benzene-d_6. To this was added 65.95 μL of hexafluoro-*tert*-butanol which had been vacuum distilled from calcium hydride. ROMP initiator **5** (32.7 mg, 0.0427 mmol) was then dissolved in 40 drops of benzene-d_6, and this yellow solution was added to the monomer solution. The reaction mixture gradually became orange and then dark reddish-brown over the course of 30 min. After 1 week, ^{1}H NMR of the reaction mixture showed that the reaction was 89% complete and that it had stopped. Benzaldehyde was added to the reaction mixture, and it was stirred for 24 h. The dark-brown reaction mixture was then pipetted into degassed methanol, and a white precipitate formed immediately. After the reaction mixture was centrifuged, the brown solvent layer was decanted off under argon. The polymer was then redissolved in benzene to yield a brown solution. Methanol was then added to precipitate the polymer, and the mixture was again centrifuged. Solvent was again decanted under argon, and the process was repeated a third time. The polymer was then dried under vacuum to yield 0.361 g of a light-green foamy solid. Yield = 85.5%. ^{1}H NMR ($CDCl_3$, all peaks were broad): δ 5.55, 5.53, 5.23, 4.95, 3.65, 3.63. ^{13}C NMR ($CDCl_3$): 167.52 m, 137−125 (m, backbone olefins), 52.27, 52.06, 41.23 m. FTIR: 3032, 2951, 2843, 1719 s, 1636, 1436, 1382, 1352, 1252, 1151, 1061, 979, 789, 754, 670 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 67.06; H, 5.91.

Poly(di-*tert*-butyl barrelene-2,3-dicarboxylate) (6b). Inside a nitrogen-filled dry box, 0.501 g (1.65 mmol) of **4b** was dissolved in 3.8 g of dry benzene. To this solution was added 56 μL of dry hexafluoro-*tert*-butanol followed by 28.2 mg of **5** dissolved in 40 drops of dry benzene. Over the course of 10 min, the reaction mixture changed color from yellow to light orange-brown. The mixture was stirred overnight, and then the reaction was quenched by adding 5 drops of degassed benzaldehyde. After this, the reaction mixture, which turned brown over 30 min, was pipetted into two centrifuge tubes, each containing 30 mL of degassed methanol. The resulting precipitate was recovered by centrifuging and was purified by repeated precipitation, as with **6a**. After drying under vacuum, 0.385 g of **6b** was obtained as a brittle light-yellow solid. Yield = 77%. *Note*: Following a smaller scale reaction by NMR shows that all monomer is consumed after 2.5 h. If any of the monomer has decomposed to form the acid, however, reaction times will be considerably longer.

^{1}H NMR: (C_6D_6, all peaks are broad) δ 5.67, 5.65, 5.54, 5.40 (4H), 4.30 (small), 3.76 (2H), 1.52 (18H); ($CDCl_3$) δ 5.52, 5.50 (2H), 5.21, 5.17 (2H), 3.95, 3.56 (2H), 1.37 (18H). ^{13}C NMR ($CDCl_3$): δ 166.19 (m, C═O), 135.33−126.22 (m, C═C), 81.33 (C of *tert*-butyl), 81.26 (C of *tert*-butyl), 41.70, 28.05 (CH_3 of *tert*-butyl). FTIR: 3006, 2979, 2933, 1716, 1674, 1636, 1477, 1456, 1393, 1368, 1351, 1273, 1256, 1155, 1087, 1060, 1034, 967, 848, 755, 667 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.48; H, 7.69.

Poly(2,3-bis((methoxy)carbonyl)phenylenevinylene) (7a). In a 50 mL round bottom flask, 100 mg (0.454 mmol) of **6a** was dissolved in 12 mL of degassed methylene chloride. To this solution was added 105.2 mg of DDQ (98% pure, 0.454 mmol) suspended in 4 mL of degassed methylene chloride. This yielded a yellow solution which was stirred under argon. During the course of the reaction, the mixture became cloudy yellow-green and eventually cloudy orange. After the mixture was stirred overnight, the reaction mixture was pipetted into a centrifuge tube containing 20 mL of degassed methanol. After centrifuging, the solvent layer was decanted, and the orange polymer that was left behind was resuspended in 10 mL of methylene chloride. Following vigorous shaking of this mixture, it was again precipitated with degassed methanol and centrifuged. Solvent was again decanted and this process was repeated one more time to yield the polymer as a fluffy orange solid. Drying the polymer yielded a dark-orange to red solid.

FTIR 3024, 2950, 1725, 1636, 1478, 1438, 1263, 1220, 1152, 1111, 1063, 1008, 959, 834, 795, 752, 702 cm^{-1}. *Note*: In some cases, adding 0.5 mL of a saturated salt solution in methanol was found to facilitate much more rapid and complete precipitation of the polymer.

Poly(2,3-bis-((*tert*-butoxy)carbonyl)phenylenevinylene) (7b). In a 50 mL RBF, 0.369 g (1.21 mmol) of **6b** was dissolved in 24 mL of degassed methylene chloride. To this light-yellow solution was added 0.281 g (98% pure, 1.21 mmol) of DDQ dissolved in 4 mL of degassed methylene chloride. The resulting yellow solution was stirred under argon overnight. During the course of the reaction, the mixture gradually became cloudy yellow and somewhat luminescent under the room lighting. After the reaction was complete, the mixture was divided in half and each half was transferred to a centrifuge tube containing 30 mL of degassed methanol. After centrifuging, the solvent was decanted and the process repeated as for **7a** until the solvent layer was clear and colorless. This usually required three to four repetitions. As before, addition of saturated sodium chloride in methanol helped faciliate precipitation. To test for complete precipitation, a sample of solvent was spotted on a nonluminescent TLC plate and exposed to a hand-held UV lamp. The absence of luminescence indicated complete precipitation of the luminescent PPV. Following purification, the polymer was dried under vacuum to yield 0.34 g of a yellow-orange solid. Yield = 93%. For preparing polymer that was 80% aromatized, the procedure was identical except that 0.8 equiv of DDQ was used. In this case, the polymer always dissolved completely in methylene chloride to yield a tranparent yellow solution during purification. ^{1}H NMR ($CDCl_3$): δ 7.66 (bs, 2H), 7.32 (bs, 2H), 1.62 (bs, 18H). ^{13}C NMR ($CDCl_3$): δ 167.05, 134.66, 133.13, 127.99, 126.74, 83.15, 28.21. FTIR: 2878, 2933, 1720, 1560,

1477, 1458, 1420, 1394, 1369, 1290, 1155, 1148, 1118, 957, 844, 824, 752, 696, 668 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 69.49; H, 7.20.

Polyphenylenevinylene Anhydride (8). This reaction was best performed by using 100% aromatized **7b** that had not been dried (i.e. it was still wet with the methanol/methylene chloride mixture). For a typical reaction, 0.35 g (1.15 mmol) of wet **7b** was transferred into a 250 mL round bottom flask with 80 mL of xylene (dry Aldrich Sure Seal). To this was added ≈40−50 mg of toluenesulfonic acid, and the yellow mixture was stirred under argon and heated to 125 °C. After the low-boiling solvent boiled off, the reaction mixture quickly changed color from yellow to bright red. Heating was continued for 12 h to ensure complete reaction, and the reaction mixture was then transferred to two 40 mL centrifuge tubes. After centrifuging, the light-brown solvent was decanted from the bright-red precipitate. The precipitate was then rinsed by shaking it with acetone and recentrifuging the mixture. After decanting the solvent, this process was repeated 2−3 more times using acetone as the solvent. The dark red solid was then dried under vacuum to yield 0.197 g of a dark-red brittle solid. Yield = 99%. This solid is only soluble in aqueous base, which opens the anhydride to yield the diacid, so it was identified by its infrared spectrum, which clearly shows the two carbonyl stretches expected of an anhydride. FTIR: 3067, 3025, 2921, 1839, 1764, 1702, 1562, 1498, 1363, 1288, 1213, 1152, 974, 923, 893, 847, 798, 753, 696, 635, 603, 574 cm^{-1}. Anal. Calcd for $C_{10}H_4O_3$: C, 69.78; H, 2.34. Found: C, 66.42; H, 2.74.

Poly(sodium phenylenevinylenedicarboxylate) (9). The sodium salt was prepared by dissolving **8** in 0.2 N aqueous NaOH. Depending on the size of pieces of **8** used, this reaction occurred nearly immediately, or it took a few hours of stirring, with the fastest reaction occurring when **8** was a fine powder. Upon reaction, the solution became the bright-yellow luminescent color of **7b**. Upon acidifying the solution with 1 M HCl, the polymer reprecipitated as an orange solid that was recollected by centrifuging the solution. FTIR of this solid showed it to be a mixture of the starting anhydride and the diacid. Precipitating the basic polymer solution by adding it into acetone, however, yielded a bright-yellow solid. After the solid was dried under vacuum, FTIR showed it to be the sodium salt **9** with some water coordinated. NMR of **9** was obtained by dissolving **7b** in 0.2 N NaOH in D_2O. ^1H NMR (D_2O): δ 7.50 (bs, 2H), 7.05 (bs, 2H). ^{13}C NMR (D_2O, CD_3OD was set at 49.00): δ 178.02, 138.39, 132.93, 128.20, 125,41. FTIR: 3416 br (coordinated H_2O), 3031, 2922, 2850, 1578, 1451, 1384, 1229, 1030, 964, 881, 831, 804, 754, 697 cm^{-1}. Anal. Calcd for $C_{10}H_4O_4Na_2 \cdot 3H_2O$: C, 41.68; H, 3.50. Found: C, 42.67; H, 3.54.

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References and Notes

(1) Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Braun, D.; Staring, E. G. J.; Demandt, R. C. J. E.; Rikken, G. L. J.; Kessener, Y. A. R. R.; Venhuizen, A. H. J. *Synth. Met.* **1994**, *66*, 75.
(3) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
(4) 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.
(5) Hide, F.; Schwartz, B. J.; Díaz-García, M. A.; Heeger, A. J. *Chem. Phys. Lett.* **1996**, *256*, 424.
(6) Parker, I. D. *J. Appl. Phys.* **1993**, *75*, 1656.
(7) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884.
(8) Wittmann, H. F.; Grüner, J.; Friend, R. H.; Spencer, G. W. C.; Moratti, S. C.; Holmes, A. B. *Adv. Mater.* **1995**, *7*, 541.
(9) Woo, H. S.; Graham, S. C.; Halliday, D. A.; Bradley, D. D. C.; Friend, R. H. *Phys. Rev. B: Solid State* **1992**, *12*, 7379.
(10) Brédas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *217*, 507.
(11) Heeger, A. J.; Long, J. *Opt. Photonics News* **1996**, *August*, 24.
(12) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
(13) Scott, J. C. *J. Appl. Phys.* **1996**, *79*, 2745.
(14) Jin, J. I.; Lee, Y. H. *Macromolecules* **1993**, *26*, 1805.
(15) Kang, I. N.; Lee, G. J.; Kim, D. H.; Shim, H. K. *Polym. Bull.* **1994**, *33*, 89.
(16) Hanack, M.; Segura, J. L.; Spreitzer, H. *Adv. Mater.* **1996**, *8*, 663.
(17) McCoy, R. K.; Karasz, F. E. *Chem. Mater.* **1991**, *3*, 941.
(18) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595.
(19) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395.
(20) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.
(21) Gorman, C. B. Ph.D. Thesis, California Institute of Technology, 1991.
(22) Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397.
(23) Conticello, V. P.; Gin, D. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 9708.
(24) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138.
(25) Wagaman, M. W. *Synth. Met.*, in press.
(26) Papadimitrakopoulos, F.; Konstadinidis, K.; Miller, T. M.; Opila, R.; Chandross, E. A.; Galvin, M. E. *Chem. Mater.* **1994**, *6*, 1563.
(27) Daub, J.; Trautz, V.; Erhardt, U. *Tetrahedron Lett.* **1972**, *43*, 4435.
(28) Daub, J.; Erhardt, U.; Kappler, J.; Trautz, V. *J. Organomet. Chem.* **1974**, *69*, 423.
(29) Cantrell, G. L.; Filler, R. *J. Org. Chem.* **1984**, *49*, 3406.
(30) Rabideau, P. W. *Org. Prep. Proced. Int.* **1986**, *18*, 113.
(31) Hales, N. J.; Heaney, H.; Hollinshead, J. H.; Singh, P. *Org. Synth.* **1979**, *59*, 71.
(32) Pu, L.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 1351.
(33) Hine, J.; Brown, J. A.; Zalkow, L. H.; Gardner, W. E.; Hine, M. *J. Am. Chem. Soc.* **1955**, *77*, 594.
(34) Ciganeck, E. *Tetrahedron Lett.* **1967**, *34*, 3321.
(35) Liu, R. H.; Krespan, C. G. *J. Org. Chem.* **1969**, *34*, 1271.
(36) Zimmerman, H. E.; Paufler, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 1514.
(37) Weber, G.; Menke, K.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 483.
(38) Block, E. *Org. React.* **1984**, 457.
(39) Mahon, M. F.; Molloy, K.; Pittol, C. A.; Pryce, R. J.; Roberts, S. M.; Ryback, G.; Sik, V.; Williams, J. O.; Winders, J. A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1255.
(40) Cotterill, I. C.; Roberts, S. M.; Williams, J. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1628.
(41) Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 1979.
(42) Schrock, R. R.; Lee, J. K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933.
(43) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.
(44) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.
(45) Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146.
(46) Wu, Z.; Grubbs, R. H. *Macromolecules* **1994**, *27*, 6700.
(47) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787.
(48) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.
(49) Webster, O. W. *Science* **1991**, *251*, 887.
(50) Mitchell, J. P.; Gibson, V. C.; Schrock, R. R. *Macromolecules* **1991**, *24*, 1220.
(51) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.
(52) Weber, G.; Menke, K.; Hopf, H. *Chem. Ber.* **1980**, *113*, 531.
(53) Böhm, I.; Herrmann, H.; Menke, K.; Hopf, H. *Chem. Ber.* **1978**, *111*, 523.
(54) Fox, H. H.; Lee, J. K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.
(55) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Zelewsky, A. V. *Coord. Chem. Rev.* **1988**, *84*, 85.
(56) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
(57) Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. W.; Miller, T. M. *Synth. Met.* **1996**, *80*, 41.
(58) Stenger-Smith, J. D.; Lenz, R. W.; Wegner, G. *Polymer* **1992**, *30*, 1048.

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