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A New Family of Highly Emissive Soluble Poly(*p*-phenylene vinylene) Derivatives. A Step toward Fully Conjugated Blue-Emitting Poly(*p*-phenylene vinylenes)

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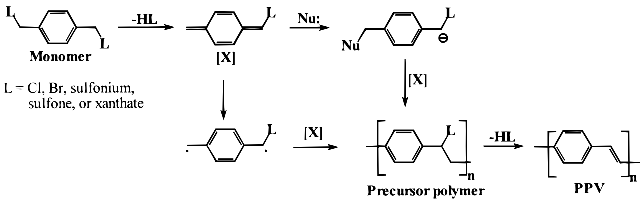
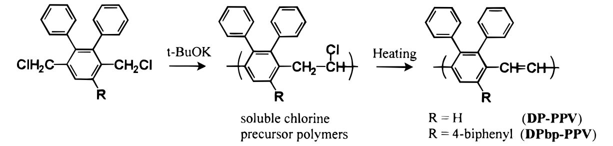
Poly(*p*-phenylene vinylene) (PPV) is the first conjugated polymer reported for the application in light-emitting diodes.[1] Today, PPV and its derivatives remain as the most popular conjugated polymer class for this application. This is due heavily to the development of several ingeniously elegant synthetic routes toward the fabrications of PPV thin films.[2] Many of these routes involve 1,6-polymerization of *p*-xylylenes to form poly(*p*-phenylene vinylenes) (PPVs).[3] A general scheme for such polymerization processes is shown in Scheme 1. The polymerization of a bis-sulfonium or a bis-halomethyl monomer in the presence of a base was reported independently in the mid-1960s.[2−4] The polymerization of sulfone or xanthate-type monomers was reported recently.[5−7] A bis-halomethyl type monomer can also be polymerized via vapor phase deposition polymerization to give a PPV.[2,3] In the case of the solution polymerization, a monomer undergoes 1,6-elimination of HL in the presence of a large excess base to form the corresponding *p*-xylylene [**X**], which undergoes radical and/or anionic 1,6-polymerization along with 1,2-elimination of HL to give a PPV. This one-step approach has been used for the synthesis of soluble PPVs with flexible side groups.[8] One can also carry out the 1,6-polymerization and the 1,2-elimination separately to obtain a soluble precursor polymer first and then cast it into thin film and convert it to the corresponding PPV. This precursor approach has been used extensively for the fabrication of insoluble PPV thin films.[2] For example, we have prepared insoluble thin films of poly(2,3-diphenyl-*p*-phenylene vinylene) (DP-PPV) and its derivatives (Scheme 2) via a chlorine precursor route (CPR).[9]

Here, we report the synthesis of the first series of a new family of soluble DP-PPV derivatives, namely poly(2,3-diphenyl-5-hexyl-*p*-phenylene vinylene) (DP6-PPV) and its derivatives via a versatile synthetic methodology that involves two key steps: first, the synthesis of new alkylated DP-PPV monomers via the Diels−Alder reaction; second, the polymerization of the monomers via a modified Gilch route involving the use of an acidic additive, such as 4-*tert*-butylbenzyl chloride.[10] Amazingly, DP6-PPV shows very high photoluminescence (PL) quantum efficiency of 65% in the solid state.

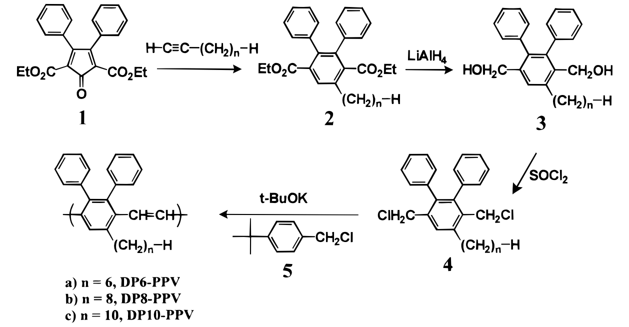
Scheme 1



Scheme 2



Scheme 3



As shown in Scheme 3, the Diels−Alder reaction of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (**1**) with 1-octyne, 1-decyne, or 1-dodecyne gives **2a**−**c** in 95−97% yields. They are reduced with $LiAlH_4$ to give **3a**−**c** and then reacted with $SOCl_2$ in methylene chloride to give monomer **4a**−**c** in 22−50% overall yields. This may be the first report on the use of the Diels−Alder reaction to introduce flexible solubilizing side groups onto monomers. Typically, flexible side groups have been introduced by alkylation of hydroxy groups [8a,11] or Ni-catalyzed coupling of an aromatic bromide with an alkyl Grignard reagent.[12] Our synthetic sequence is very versatile and offers the possibility of introducing virtually any functional group or chromophore into 1,4-bis(chloromethyl)benzene monomers routinely.[9] With a simple access to a wide range of monomers, DP-PPV derivatives are becoming the most fertile family of PPV derivatives.

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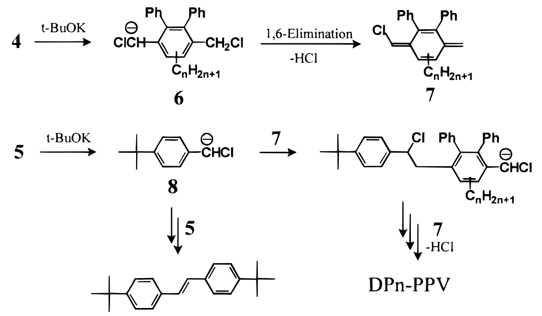
Table 1. Polymerization Parameters and the Molecular Weights of DP*n*-PPVs

	monomer	**5**/**4**//THF (mg/g//mL)	molar ratio **5**:**4**	1.0 M *t*-BuOK in THF (mL)[a]	M_w/M_n ($\times 10^3$)[b]	PD	yield
1	**4a**−**c**	0.0/0.3//15		4.4	gel		
2	**4a**	7.5/0.3//15	0.056	4.4	>2000		71
3	**4a**	67/0.3//15	0.51	4.4	1060/330	3.20	66
4	**4a**	89/0.3//15	0.67	4.4	988/300	3.29	50
5	**4a**	133/0.3/15	1.00	4.4	350/110	3.18	45
6	**4b**	136/0.33//15	1.00	4.4	571/150	3.80	40
7	**4c**	182/0.47/16	1.00	4.4	404/123	3.28	71

[a] The base was added all at once into an ice−water-cooled and magnetically stirred solution of **5**/**4**//THF. [b] Relative to polystyrene in CH_3Cl.

Scheme 4



As shown in Table 1, entry 1, a typical Gilch route that involves the polymerization of **4a**−**c** with a large excess of *t*-BuOK gives insoluble DP*n*-PPV gels. We overcame this problem by using a modified Gilch route involving the use of a nonpolymerizable acidic additive in the polymerization.[10] Entries 2−5 using *tert*-butylbenzyl chloride (**5**) as the acidic additive, show that soluble high molecular weight DP6-PPVs with relatively narrow molecular weight distribution are obtained. Similarly, soluble DP8-PPV (entry 6) and DP10-PPV (entry 7) were prepared. The molecular weight of DP6-PPV decreases as the molar ratio of **5**:**4a** increases. This can be accounted for by the anionic polymerization mechanism shown in Scheme 4. Deprotonation of a chloromethyl proton in **4** gives an anionic intermediate **6**, which undergoes a 1,6-dehydrochlorination to give *p*-xylylene **7**. Deprotonation of **5** produces **8**, which can nucleophilically attack **7** to initiate anionic polymerization to give DP*n*-PPV with *tert*-butyl chain ends or attack **5** followed by 1,2-dehydrochlorination to give 4,4′-di-*tert*-butylstilbene as a side product.[4b] The formation of the stilbene is one possible reason for the formation of high polymers even in the presence of a large amount of **5**. The other possibility is the involvement of radical polymerization of **7** as reported for the analogous sulfonium precursor routes and sulfone precursor routes.[13,14]

Although the soluble DP-PPV derivatives shown in Table 1, entries 2−7, were isolated by a single precipitation of the reaction mixtures into methanol, they still showed very high purity according to elemental analysis. For example, DP6-PPV shows that elemental analysis data of C 90.47, H 7.53, Cl 0.14 are in agreement with C 92.26, H 7.74 as calculated for $[C_{26}H_{26}]_n$. This result indicates that the soluble DP6-PPVs obtained from the modified Gilch route have very high purity and very low chlorine content, which implies a high degree of conversion of greater than 99.0%.

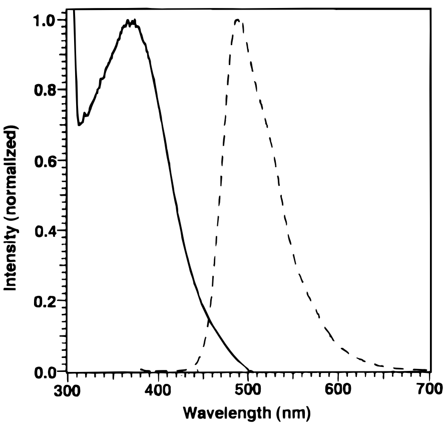


Figure 1. UV−vis (solid line) and photoluminescence (PL) (dotted line) spectra of a DP6−PPV thin film (intensities are normalized).

The UV−vis and PL spectra of a DP6-PPV thin film are shown in Figure 1. The bluish-green emission peak at 490 nm for DP6-PPV is about 10 nm blue shifted with respect to that of DP-PPV.[9b] This is attributable to the steric effect of the *n*-hexyl group that reduces the effective conjugation length. To our best knowledge, the 490 nm emission for DP6-PPV is the bluest PL emission for a fully conjugated PPV. Through the introduction of more steric hindrance, a blue emitting (<480 nm), fully conjugated PPV may be possible. This intriguing possibility is being explored in our laboratory. Blue-emitting materials are particularly useful for designing multiccolor electroluminescent devices.[15]

Excited at 370 nm, DP6-PPV thin films showed a very high PL quantum efficiency of 65%. This is one of the highest PL efficiencies reported for PPVs. For comparison, the solid-state PL efficiencies for PPV, poly(2-methoxy-5-((2′-ethylhexyl)oxy)-*p*-phenylene vinylene) (MEH-PPV), poly((2-dimethyloctyl)silyl-*p*-phenylene vinylene) are 15, 27, and 60%, respectively.[16] The high PL quantum efficiency for DP6-PPV may be due to the steric effect of the two phenyl rings and the alkyl groups, which can prevent self-quenching processes, induced by closely packed emissive segments.[17] It has been reported that closely packed conjugated polymers are prone to the formation of exciplexes or polaron pairs that can serve as quenching sites.[17]

In summary, we have reported the synthesis of DP6-PPV, DP8-PPV, and DP10-PPV as the first series of a new family of soluble, highly emissive DP-PPV derivatives. The key synthetic steps are the monomer synthesis via the Diels−Alder reaction and the polymerization via a modified Gilch route involving an anionic polymerization mechanism. The polymers were obtained in 40−70% yields and showed very high molecular weights and purity. The PL emission peak of 490 nm may represent the bluest emission peak reported for a fully conjugated PPV. The PL efficiency of 65% for DP6-PPV is among the highest values reported for a fully conjugated PPV.

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Supporting Information Available: Experimental details (5 pages). See any current masthead page for ordering and Internet access instructions.

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