Poly(phenylenevinylene)s with Dendritic Side Chains: Synthesis, Self-Ordering, and Liquid Crystalline Properties

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Poly(phenylenevinylene) (PPV) and its derivatives are an interesting class of polymers that have many applications as active materials in optoelectronic devices.[1−3] PPV without any substituents is insoluble in organic solvents and is usually processed from its precursor polymer followed by a conversion reaction. Various side chains can be attached to the PPV backbone to render it soluble and processable. Commonly used side chains are simple linear alkyl and alkoxy substituents. These polymers are classified as "hairy rod" polymers and have been found to be thermotropic liquid crystals.[4,5] However, these types of polymers tend to form aggregates and result in low photoluminescence and electroluminescence quantum efficiencies due to aggregation quenching.[6] To solve this problem, branched chains, such as 2-ethylhexyloxy in poly(2-methoxy-5-(2-ethylhexyloxy)-phenylenevinylene) (MEH-PPV), and bulky substituents[7−9] have been used. Other approaches involve the formation of nanosized PPV domains by self-assembly[10] or use of liquid crystals as templates.[11] In addition, dilution of PPV chromophores using block copolymers or polymer blends[12] and deliberate inclusion of *cis*-PPV are effective methods.[13] In this paper, we report the synthesis and structural characterization of branched and hyperbranched (dendritic) side chain substituted PPVs. Bulky side chains are used to enhance main-chain PPV separations in the solid state. Interestingly, these polymers were found to exhibit thermotropic liquid crystalline order. Liquid crystallinity could be used to form highly ordered photoluminescent films for generating polarized light.[4]

The dendritic side chain used here is similar to those developed by Percec et al. as shown in Scheme 1.[14] Methyl-3,4,5-trihydroxybenzoate was chosen as the core for building up the dendritic side chains since highly branched molecules can be formed from it even at low generations.[14] The chemical structures and syntheses of the polymers are also shown in Scheme 1.[5] The elemental analysis results are given in the reference section.[15,16] Palladium-catalyzed Heck reactions are used for the polymerizations.[5,17,18] The Heck reaction was previously found to have side reactions where both the 1- and 2-position of the vinyl group can react with phenyl halides with much lower reactivity at the 2-position.[17] In our case, the vinyl groups due to this side reaction were barely visible in ^{1}H NMR, and subsequent observations of self-ordering and liquid crystalline properties of these polymers indicate that few structural defects should exist.

Our two polymers, namely PPVD0 and PPVD1 as shown in Scheme 1, are soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene. The relative molecular weights (MWs) of these polymers were determined by gel permeation chromatography (GPC) using THF as eluent and calibrated with polystyrene standards at 35 °C.[16] Both PPVD0 and PPVD1 have reasonable MWs greater than 10 kDa. The absolute MW was also determined for PPVD1 with laser light scattering measurements and was found to be about 2 times higher than its relative MW as determined by GPC. The number of repeating units calculated from its absolute number-average MW is about 15.

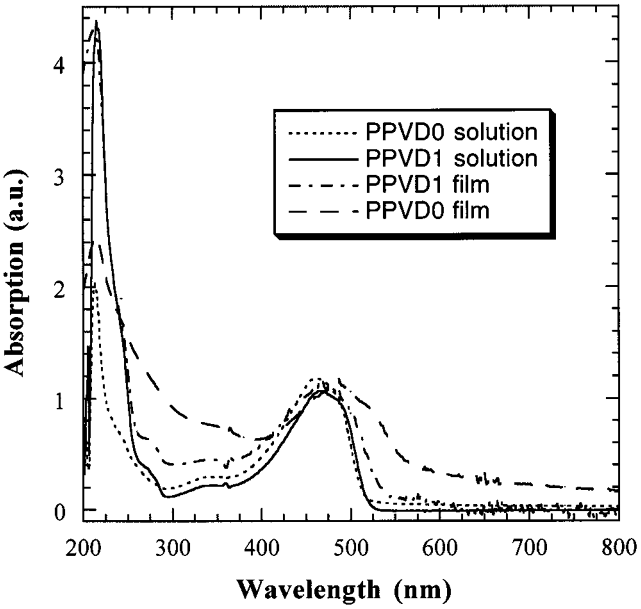

Figure 1. UV−vis spectra of PPVD0 and PPVD1 in THF solutions and from thin films.

The UV−vis absorption spectra were measured for both solutions (in THF) and thin films (Figure 1). PPVD0 and PPVD1 have similar absorption spectra in solution characterized by maximum absorption (λ_{max}) at around 215 nm, resulting from the $\pi-\pi^*$ transition of isolated phenyl rings from the side chains, and at 460 nm due to the $\pi-\pi^*$ transition of the PPV backbone. The spectrum of a PPVD1 film prepared from evaporation of THF solvent has the same λ_{max} as its solution spectrum but with slightly broadened absorption line width. The fact that λ_{max} remains unshifted indicates weak interactions between the conjugated backbones in the solid state, possibly due to the bulky dendritic side chains. Different from PPVD1, the spectrum of PPVD0 film is red-shifted compared to its spectrum in THF solution, which is commonly observed for alkyl-substituted PPVs resulting from $\pi-\pi$ stacking of the conjugated backbones.[6]

X-ray diffraction measurements have been performed on films prepared from different solvents (Figure 2). Both polymers were found to self-order with polymer backbones parallel to the substrate and with a strong solvent dependence of the degree of ordering. For a PPVD0 film cast from chloroform at room temperature, a very sharp diffraction peak was found at $2\theta = 2.32°$ ($d = 38$ Å), and higher orders were also visible, indicating very high degree of ordering under this condition. However, when toluene was used as the solvent and evaporated at about 50 °C, a diffuse peak was found at

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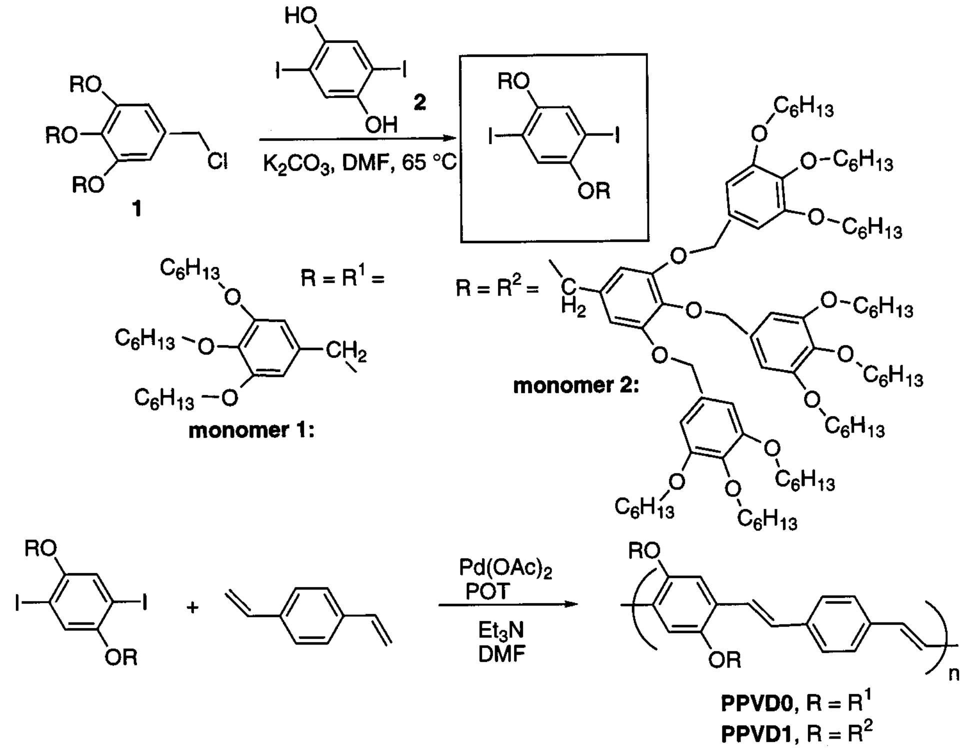
Scheme 1. Syntheses of Monomers and Polymers



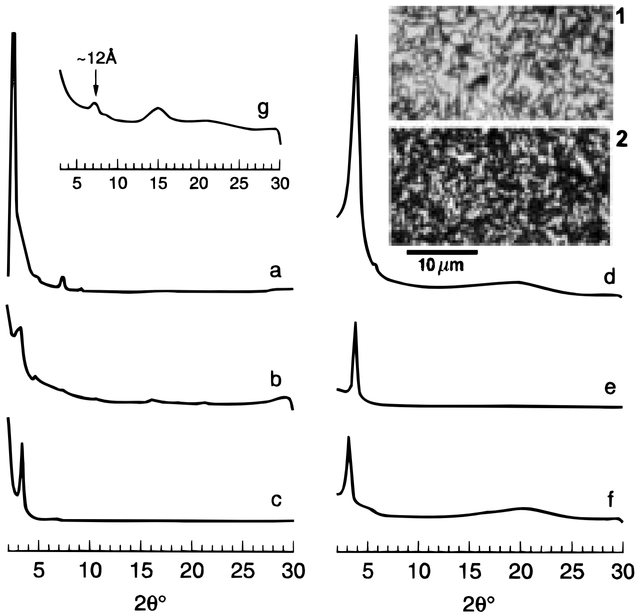


Figure 2. X-ray diffraction patterns of PPVD0 and PPVD1 films prepared from different solvents. (a) PPVD0 cast from chloroform solution at room temperature; (b) PPVD0 cast from toluene solution at 50 °C; (c) PPVD0 cast from 1,1,2,2-tetrachloroethane solution at 50 °C; (d) PPVD1 cast from chloroform solution at room temperature; (e) PPVD1 cast from toluene solution at 50 °C; (f) PPVD1 cast from 1,1,2,2-tetrachloroethane solution at 50 °C; (g) PPV7 cast from chloroform solution at room temperature. Inset: polarized optical photographs showing the typical schlieren texture for (1) PPVD0 and (2) PPVD1.

$2\theta = 3.35{-}3.55°$ corresponding to a spacing of 25–26 Å. A much narrower and intense diffraction peak at $2\theta = 3.55°$ ($d = 25$ Å) was found for a film cast from 1,1,2,2-tetrachloroethane at 50 °C. The 25 and 38 Å spacings may represent the backbone separations for two alternative forms of interdigitation. The 38 Å distance would be very reasonable for extended side chains essantially transverse to the PPV backbone with little or no interdigitation.

For PPVD1, similar spacings ca. 22–26 Å were observed for all films prepared from different solvents except that the diffraction peak appeared to broaden for the film prepared from chloroform solution while it was narrower from toluene and 1,1,2,2-tetrachloroethane. This spacing corresponds approximately to the radius of the dendritic side chain; this result therefore indicates that the side chains of PPVD1 are interdigitated in the solid state. The X-ray diffraction pattern for a diheptoxy-substituted PPV (**PPV7**) prepared using the same polymerization reaction was also obtained for comparison. However, only diffuse peaks were seen for the film cast from chloroform solution. Therefore, the bulky dendritic side chains seem to be much more effective in promoting self-ordering in these PPV derivatives. A similar effect has been found to facilitate the self-assembly of flexible random-coil polymers with dendritic side groups.[19] We are currently synthesizing different types of dendritic side chains to investigate this effect further. A related system has also been previously reported which has a rigid poly(phenylene) backbone with polyaryl ether dendrons (e.g., Frechet-type dendrons)[20] as side chains.[21] This polymer was found to self-assemble into nanostructures on highly oriented pyrolytic graphite. However, no X-ray results on solution cast films or any liquid crystalline properties have been reported.

Notably, both PPVD0 and PPVD1 were found to exhibit thermotropic nematic liquid crystal phases. Thin films cast from THF were studied by optical microscopy. Images as viewed between crossed polarizers are shown in Figure 2, insets 1 and 2. Brightness arises from the birefringence of the liquid crystal state, and the numerous threadlike dark lines are typical of the schlieren texture of nematics. To verify that the nematic phase is not related to the solvent used to cast the films, another set of films were spin coated on glass. In this case, the solvent evaporates so quickly that the films appear amorphous at room temperature. However, upon heating the films to around 180 °C and then cooling, Schlieren texture spontaneously forms. This shows that the nematic state is thermodynamically preferred in the absence of solvent. The nematic-to-isotropic transition temperature (T_{NI}) was measured on much thicker speciments ($\sim$10−15 μm) to avoid finite thickness effects and to give a strong birefringence signal. Upon heating, the birefringence fades and the field eventually becomes dark between crossed polarizers. Upon cooling the birefringence returns. From these observations, the nematic-to-isotropic transition temperature was determined to be 200 ± 5 °C for PPVD0 and 211 ± 5 °C for PPVD1. The nematic character of PPV derivatives can be exploited in a number of ways to generate strongly aligned films, resulting in enhanced photoconductivity and better charge transport capability, as well as polarized light emission.[4,22,23] For example, the polymers can be strongly aligned by deformation. After a thin film of either material is sheared, it exhibits a persistent birefringence with few defects. In addition, anisotropic absorption of sheared film using polarized light source was observed. This reflects a high degree of polymer chain alignment.

Among conjugated polymers, liquid crystallinity is common for the "hairy rod" polymers, which have rigid backbones and flexible side chains.[4,5,24] This work may be the first that reports a LC phase for conjugated polymers with bulky dendritic substituents. To a certain degree, these dendritic side chains are also internally flexible. However, compared to linear alkyl chains, they are much bulkier and the resulting interchain packings are expected to be more sensitive to their spatial shapes. It should be pointed out that liquid crystalline properties have previously been observed with dendrimers.[25,26] Studies are being carried out to investigate the generality of the above observations for dendrimer-substituted conjugated polymers and the effects of the nature of the dendrimer (number of generation, shape, etc.) on self-ordering and liquid crystalline properties.

In conclusion, we have synthesized new types of poly(phenylenevinylene) substituted with dendritic side chains. These polymers were found to self-order in the solid state and yield thermotropic nematic phases. These PPVs are currently being investigated as light-emitting materials in electroluminescent devices. We do not expect that these polymers will be ideal single-layer electroluminescent materials since they contain large insulating side groups. However, similar polymers with electron- or hole-transporting side chains arranged in a dendritic fashion may possess interesting electroluminescent properties.

Supporting Information Available: Supprting Information Available: NMR spectra for monomers and polymers (9 pages). Ordering information is given on any current masthead page.

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(15) The general procedures for monomer syntheses can be found in ref 14. Compound **2** was synthesized according to the following reference: Peng, Z.; Gharavi, A.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622−4632. Monomer 1, calcd for $C_{56}H_{88}I_2O_8$: C, 58.84; H, 7.76. Found: C, 59.16; H, 7.68. Mp 63−66 °C. ^{1}H NMR ($CDCl_3$) s 0.89 (t, CH_3, 18H), 1.32 (m, CH_2, 24H), 1.47 (m, CH_2, 12H), 1.78 (m, CH_2, 12H), 3.97 (t, OCH_2, 12H), 4.96 (s, OCH_2-Ph, 4H), 6.68 (s, phenyl, 4H), 7.28 (s, phenyl, 2H) ppm. Monomer 2, calcd for $C_{170}H_{268}O_{26}I_2$: C, 68.48; H, 9.06. Found: C, 68.80; H, 8.87. Mp 73−76 °C. ^{1}H NMR ($CDCl_3$) s 0.88 (t, CH_3, 54H), 1.31 (m, CH_2, 72H), 1.41 (m, CH_2, 36H), 1.71 (m, CH_2, 36H), 3.79 (t, OCH_2, 12H), 3.89 (m, OCH_2, 24H), 4.92 (s, OCH_2-Ph, 4H), 4.99 (s, OCH_2-Ph, 4H), 5.04 (s, OCH_2-Ph, 8H), 6.63 (s, phenyl, 8H), 6.65 (s, phenyl, 4H), 6.82 (s, phenyl, 4H), 7.26 (s, phenyl, 2H) ppm.
(16) Elemental analysis for PPVD0, calcd for $C_{66}H_{96}O_8$: C, 77.91; H, 9.51. Found: C, 77.28; H, 9.36. PPVD1, calcd for $C_{180}H_{276}O_{26}$: C, 75.70; H, 9.74. Found: C, 75.49; H, 9.57. GPC results for PPVD0, weight-average molecular weight (M_w) = 25.3 kDa; polydispersity (disp) = 2.31. PPVD1, M_w = 34.5 kDa; disp = 1.55. Molecular weight determined by laser light scattering for PPVD1, M_w = 62.8 kDa; disp = 1.55.
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