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Photoluminescence properties of polynaphthalenevinylene (PNV) homopolymers and block copolymers by ring-opening metathesis polymerization (ROMP) and study of their photoluminescence properties

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Well-defined transition metal catalysts have been developed over the last few years for the precise synthesis of polymers. Many of these catalysts are living and can be used to prepare near monodispersed homopolymers and block copolymers. Ring opening metathesis polymerization (ROMP) initiators have been developed that will tolerate a wide range of functionalities and reaction conditions. A family of barrelene and barrelene derivatives have been prepared which can be ROMP'd to precursors to poly(phenylenevinylene) and poly(naphthylenevinylene). Using newly developed techniques, these monomers are being polymerized to form block polymers that contain monomers which give homopolymers with different emission spectra. The effects of phase separation and spectral matching are being investigated.

1. Introduction

The discovery of electroluminescence in polyphenylenevinylene PPV (Burroughes *et al.* 1990) prompted an expansion in the field of conjugated polymers to further explore this phenomenon and to synthesize new materials which also exhibit this property. While convenient routes exist for the synthesis of many conjugated polymers including polyacetylene (PA), PPV and polyparaphenylene (PPP) (Skotheim 1986), more convenient syntheses of these polymers and their derivatives are required to fully explore their electroluminescence properties. Two areas which are of special interest are the ability to tune the luminescence colour and also to improve the polymer's quantum yield. To accomplish these goals, syntheses which allow the addition of electron donating or withdrawing groups are desired, since such substituents can be used to tune the bandgap of conjugated polymers (Brédas & Heeger 1994; Meyers *et al.* 1993). Changing the bandgap not only causes a shift in the luminescence colour, but may also improve efficiency by placing the polymer's conduction and/or valence bands closer to the work functions of the electrodes, thereby making electron and hole injecting easier. These goals may also be accomplished by random and

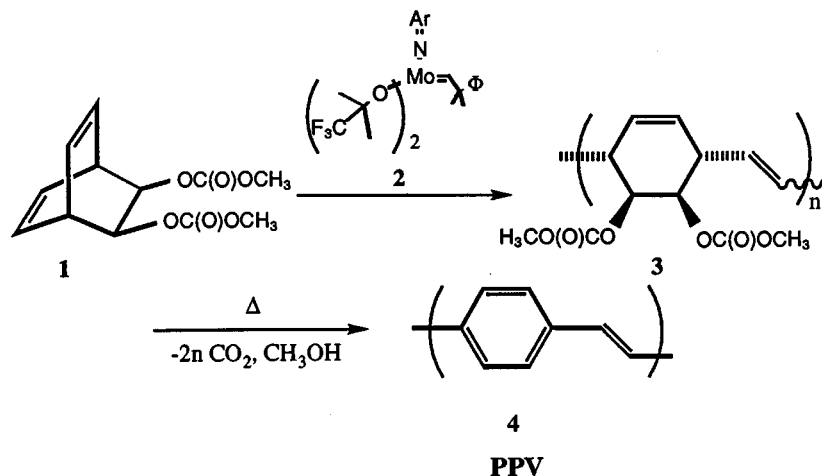
block copolymers. Random copolymers shift the bandgap relative to the homopolymers by averaging the bandgaps of the two polymers. Block copolymers on the other hand, can contain two polymers with different bandgaps. Ideally, one of the blocks matches the electron injection electrode and the other matches the hole injection electrode. Excitons formed in the two blocks then migrate to the section with the smaller bandgap and luminesce from there, thus increasing the total output of that section. However, while the synthesis of random copolymers is relatively simple, the synthesis of block copolymers is difficult by most of the methods employed to synthesize conjugated polymers. As a result, these methods typically yield poorly defined block copolymers. An additional advantage is gained if the polymers can be made soluble so that electroluminescent (EL) devices can be fabricated more easily.

In the past we have shown that conjugated and electroluminescent polymers can be synthesized by ring-opening metathesis polymerization (ROMP), either directly or through a precursor route (Gorman 1991; Gorman *et al.* 1993; Klavetter & Grubbs 1988; Conticello *et al.* 1992). The use of ROMP to make these polymers affords several advantages over other polymerization methods. First, ROMP is conducive to the synthesis of conjugated polymers, since olefin bonds in the monomer are not consumed but rather become part of the polymer backbone. Therefore, by using a properly designed monomer, a polymer which is fully conjugated or can be converted to a fully conjugated polymer is readily formed. Olefin metathesis also has the advantage of being quite mild so that polymer degradation, which can occur in polymerization methods requiring harsher conditions or high temperature, is minimized. Because they often yield living polymerizations, well-defined ROMP catalysts also allow good control of molecular weight and the synthesis of monodisperse polymers. Such control permits the synthesis of homopolymers with consistent properties, but more importantly, living ROMP allows well-defined block copolymers to be readily synthesized by sequential monomer addition. Since ROMP is more tolerant to different functionalities than other polymerization types, it is also an important tool which expands the variety of polymers that can be synthesized. With the mild conditions and good control of living ROMP, both homopolymers and block copolymers which would be difficult to synthesize by other methods can be prepared.

The first synthesis of PA by a ROMP precursor route was reported by Edwards & Feast (Edwards & Feast 1980; Edwards *et al.* 1984; Bott *et al.* 1986). This route afforded PA via a retro Diels–Alder reaction upon heating of the ROMP precursor polymer. We later showed that PA can be synthesized directly by the ROMP of cyclooctatetraene (COT) (Klavetter & Grubbs 1988), and soluble derivatives can be obtained by the ROMP of alkylated COTs (Gorman 1991; Gorman *et al.* 1993). Our first synthesis of an electroluminescent polymer by ROMP yielded PPV by aromatization of a precursor polymer (Conticello *et al.* 1992). First, a barrelene-like monomer containing acetate groups, **1**, was polymerized with the ROMP initiator, **2**, as shown in scheme 1. As with the synthesis of PPP which we reported earlier (Gin *et al.* 1992), the precursor polymer, **3**, which was solubilized by the acetate groups and therefore easily processible, was cast into a film and this film was then converted to PPV by base catalysed, thermal elimination of the acetate moieties. More recently, we reported a similar synthesis to yield soluble polynaphthalenevinylene (PNV) by a precursor route (Pu *et al.* 1996). In this case, benzobarrelene monomers with alkyl groups attached, were polymerized using a similar molybdenum initiator, $\text{Mo}(=\text{NAR})(\text{OC}(\text{CF}_3)_2\text{CH}_3)(=\text{CHC}(\text{CH}_3)_2\Phi)$, **5**. Using DDQ as the oxidant, the precursor polymers were then aromatized in solution at room temperature to yield

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Scheme 1. Synthesis of PPV by a ROMP precursor route.

PNVs which were soluble in organic solvents. The polymerizations of monomer **1** and the benzobarrelene monomers were not living, however, and therefore the reaction was not conducive to block copolymer formation.

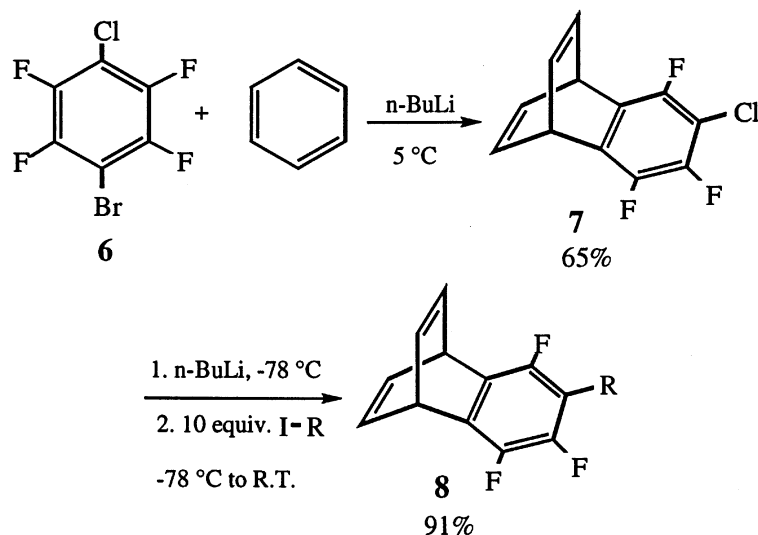
We now report that **5** can be activated to yield a living polymerization system for benzobarrelenes that not only yields well-defined monodisperse homopolymers, but also can produce well-defined block copolymers. Using this system, we have synthesized a series of PNV homopolymers which show that the presence of halogen substituents causes a shift in the photoluminescence emission wavelength. A PNV diblock copolymer was also studied and found to show luminescence only from the segment with the smaller bandgap. We also developed a new synthesis of alkylated benzobarrelene monomers which yields large quantities of both the halogenated and unhalogenated monomers from relatively cheap starting materials in fewer steps than the synthesis we previously reported.

2. Results

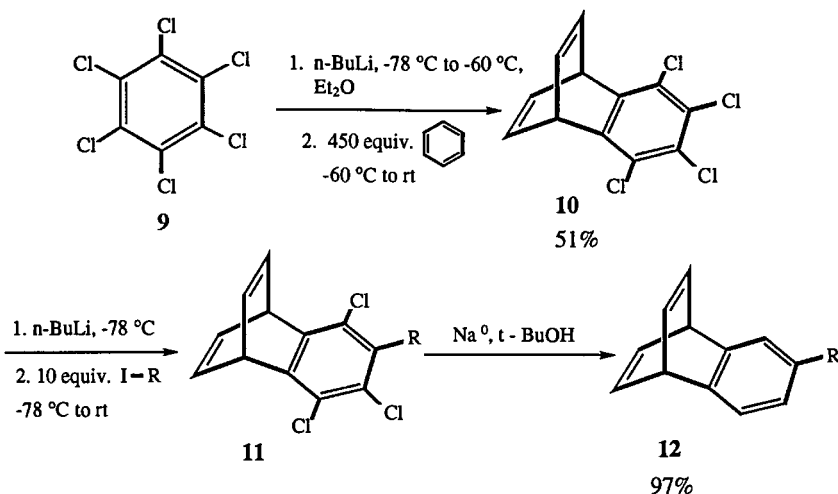
(a) Monomer synthesis

We previously reported the synthesis of alkylated benzobarrelenes using a protected diol benzene equivalent (Pu *et al.* 1996; Pu & Grubbs 1994). Since attempts to apply this method to the synthesis of a trifluoroalkylbenzobarrelene monomer failed, a new synthesis was developed for this monomer. As shown in scheme 2, 1-bromo-4-chloro-2,3,5,6-tetrafluorobenzene, **6**, reacts with butyl lithium to yield a benzyne intermediate which reacts with benzene to yield the Diels–Alder adduct. Following purification, a second metal halide exchange using butyl lithium at low temperature yielded the lithium adduct. Addition of an excess of alkyl iodide and gradual warming to room temperature afforded the alkylated benzobarrelene, **8**.

Alkylated trichlorobenzobarrelene was synthesized by a similar route, shown in scheme 3. In this case, lithiumpentachlorobenzene was formed at low temperature. The benzyne then formed and underwent a Diels–Alder reaction with benzene as the reaction mixture was warmed (Hales *et al.* 1979). Alkylation of tetrachlorobenzobarrelene was then performed under conditions identical to those used for formation of trifluoroalkylbenzobarrelene. As shown in table 1, both **7** and **10** were alkylated



Scheme 2. Synthesis of 3,4,6-trifluoro-5-alkylbenzobarrelene.



Scheme 3. Synthesis of trichloro-4-alkylbenzobarrelene and 4-alkylbenzobarrelene.

with a series of linear and branched alkyl iodides. The yields of these reactions were usually high with only the desired product being visible by ^1H NMR in most cases. In the case of the α -substituted iodide, **11d**, the yield was quite poor, probably as a result of the competing elimination reaction.

The unhalogenated octylbenzobarrelene, **12**, was then obtained from **11a** in 97% yield by removal of the chlorines as reported for tetrachlorobenzobarrelene (Hales *et al.* 1979). Comparison of the ^1H NMR of alkylbenzobarrelene prepared by this method and by the previously reported method (Pu *et al.* 1994; Pu & Grubbs 1994), which can only yield 4-alkylbenzobarrelene, shows that the new method also yields benzobarrelenes alkylated only in the 4 position. So overall, the synthesis presented here not only allows the synthesis of alkylated benzobarrelenes containing halogen substituents, but also provides an efficient synthesis of 4-alkylbenzobarrelene from

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Table 1. Yields for synthesis of trihalobenzobarrelenes **8** and **11**

(All yields are isolated yields following distillation of excess iodide and column chromatography except for entry **11d** which was determined on the crude reaction mixture by GC/MS.)

product	alkyl iodide	% yield
8a	I(CH ₂) ₃ CH ₃	88
8b	I(CH ₂) ₇ CH ₃	91
8c	I(CH ₂) ₂ CH(CH ₃) ₂	83
11a	I(CH ₂) ₇ CH ₃	78
11b	I(CH ₂) ₂ CH(CH ₃) ₂	86
11c	I(CH ₂) ₂ CH(CH ₃)(CH ₂) ₃ CH(CH ₃) ₂	90
11d	ICH ₂ CH(CH ₂ CH ₃)(CH ₂) ₃ CH ₃	10

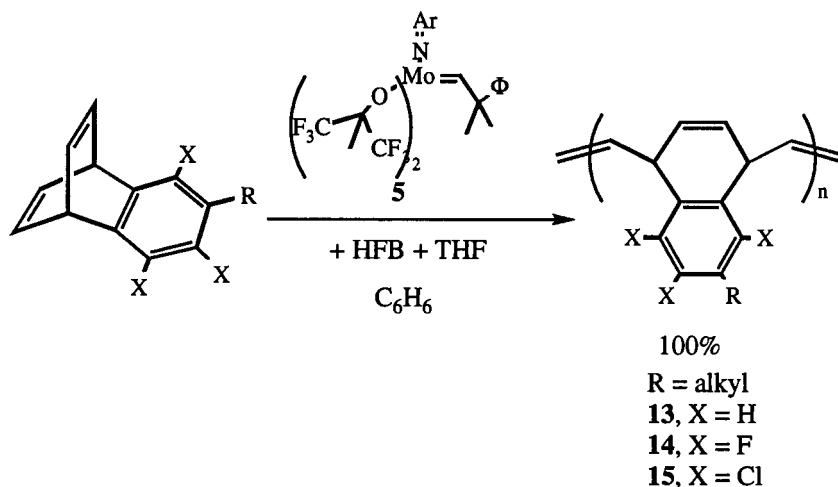
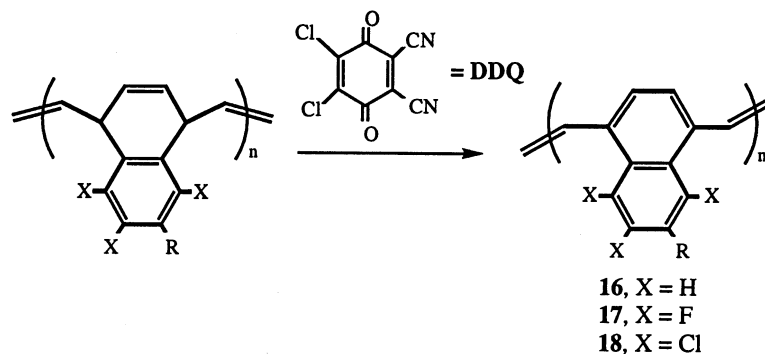
inexpensive starting materials. Previous attempts to alkylate tetrachlorobenzobarrelene by nucleophilic attack by Grignards, Heck coupling and attack of Grignard reagents by a benzyne intermediate failed, further emphasizing the success of the alkylation presented here.

(b) Polymer synthesis

The synthesis we reported for alkylated-PNV was sufficient to obtain the desired homopolymers, but a more reliable, living system was desired to yield more homogeneous homopolymers and block copolymers. While **5** alone does not initiate well—no propagating carbene signal can be observed by ¹H NMR—it was found that hexafluoro-*t*-butanol (HFB) activates the catalyst and propagating carbene is observed. In the case of **11a**, full initiation is observed at a monomer to catalyst ratio of 25 but, with **8** and **12**, full initiation is achieved only when the monomer to catalyst ratio is 100 or greater. Increasing the total concentration of both reactants, monomer and catalyst, also did not effect full initiation when the monomer to catalyst ratio was kept below 100. Addition of 10 equivalents of THF relative to catalyst, however, was found to effect full initiation at lower monomer to catalyst ratios for both of these monomers. THF slows the rate of the overall reaction, but slows propagation more than initiation so that full initiation of **5** is achieved.

In all cases, addition of alcohol was found to significantly reduce the PDI of the polymers obtained from PDI = 3–5, with 0 equivalents of alcohol added, to PDI = 1.1–1.8, with 15 equivalents of alcohol added. In the cases where THF was added, the PDI was reduced further to yield polymers **13** and **14**, shown in scheme 4, with PDIs of 1.2 and 1.4, respectively. Using this alcohol activated, THF deactivated system, benzobarrelene block copolymers were synthesized by sequential monomer addition.

As previously reported, the polymers were aromatized in solution using DDQ to yield the conjugated polymers **16**, **17** and **18**, as shown in scheme 5. In the case of the halogenated polymers, longer reaction times or higher temperatures were required for complete reaction. Polymers **13** and **14** were aromatized at room temperature in methylene chloride. The reaction mixture containing **13** turned the deep red colour of PNV immediately upon addition of DDQ and the oxidation was complete after 3 hours. Polymer **14** took longer to oxidize, but the reaction was complete after stirring overnight. Oxidation of **15** takes several days in hot methylene chloride or overnight in toluene or chlorobenzene at 110–120 °C. Due to the similar susceptibility

Scheme 4. Polymerization of benzobarrelenes by **5** in the presence of HFB and THF.

Scheme 5. Aromatization of precursor polymers.

to aromatization by DDQ of their precursor polymers and their comparable fluorescence intensities, a block copolymer consisting of a PNV block and a trifluoro-PNV block, **19**, was also studied.

(c) Photoluminescence measurements

Following purification of the conjugated polymers, photoluminescence data were collected for solutions of the polymers in chloroform. As shown in table 2, the photoluminescence emission wavelength of the halogenated polymers was red shifted relative to that of the PNV studied. The red shift observed is consistent with a stabilization of the LUMO predicted by theoretical calculations and experimental observations for other conjugated polymers containing electron withdrawing groups (Brédas & Heeger 1994). Calculations done by Brédas & Cornil (personal communication[†]) for polymer **17** studied here also predict that the LUMO is stabilized more than the HOMO, resulting in a smaller bandgap and a red shift of the emission wavelength.

[†] Their calculations show an E_g of 3.43 eV for **16** and 3.37 eV for **17**. Calculations were first done to optimize the geometries of hexamers of the hopolymers and a block copolymer using a semi empirical Hartree–Fock Austin Model 1 (AM1) method. E_g values were then determined by INDO/SCI (intermediate neglect of differential overlap coupled to a single configuration interaction scheme) calculations.

Table 2. Photoluminescence measurements of PNV homopolymers and a PNV block copolymer in solutions of chloroform

polymer	λ_{ex}	λ_{em}	relative intensity
16	403	551	2.5
	485 ^a	561	3.3
17	403 ^a	568	0.42
	485	579	0.22
18	440 ^a	569	93.2 ^b
19	403	568	1.5
	485 ^a	577	2.7

^a the excitation maximum;

^b indicates that this measurement was done at 1/25 the concentration of the others and the intensity was multiplied by 25.

A somewhat unexpected result was that the emission intensity of **17** was much less than that of **16**, while the intensity of the **18** was much greater than that of **16**.

Study of a solution of block copolymer **19** showed that the emission maximum of this polymer is at the same wavelength as homopolymer **17**, but that the emission intensity mimics that of homopolymer **16**. These measurements suggest that any excitons formed in the PNV block are transferred to the trifluoro-PNV block, the segment with the smaller bandgap, and luminesce from there. While this energy transfer occurs in the block copolymer, no energy transfer between polymers is observed in a solution containing a 1:1 mixture of homopolymers **16** and **17**. For the homopolymer mixture, the luminescence of polymer **16** dominates the spectrum because the polymer **17**'s luminescence is much weaker. Energy transfer in block copolymers has been predicted by theoretical calculations of other conjugated polymers, and recent calculations on the polymers studied here also predict that excitons should migrate to the trifluoro-PNV block of polymer **19** (Brédas & Heeger 1994; Meyers *et al.* 1993).

3. Conclusions

A series of PNV homopolymers and copolymers were synthesized by a ROMP precursor route. First, a new monomer synthesis was developed to allow synthesis of benzobarrelene monomers containing halogen substituents. Using a polymerization system based on initiator **5** with HFB and THF to yield a more controlled polymerization, these monomers were polymerized to produce precursor homopolymers and block copolymers. Aromatization of these polymers in solution under mild conditions gave the fully conjugated polymers.

Study of the PNVs with and without halogen substituents showed that the electron withdrawing groups caused a red shift in the photoluminescence of the PNV homopolymers. This red shift is consistent with theory which predicts that electron withdrawing substituents should stabilize the LUMO more than the HOMO, therefore producing a smaller bandgap. A block copolymer **19**, containing a PNV block

and a trifluoro-PNV block, showed luminescence with the same wavelength as the trifluoro-PNV homopolymer, **17**, but with the intensity characteristic of the PNV homopolymer, **16**. This observation, which is also consistent with theory, suggests that excitons formed in the PNV block, which has a larger bandgap, migrate to the trifluoro-PNV block, which has a smaller bandgap, before luminescing.

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