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# A modified Wittig polycondensation—to high-*trans*- and high-molecular weight PPVs

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**Abstract**—A modified Wittig polycondensation was developed by replacing the bulky $-PPh_3$ with $-PBu_3$ ylide. Our studies suggested that the modified polymerization dramatically enhances *trans*-selectivity due to the decreased 1,3-steric interaction between butyl chain and triphenylamine group, together with the 1,2-steric interaction between the phenyl ring of the ylide and the triphenylamine group of the aldehyde. Moreover, the method also enhances high-molecular weight products by increasing the activity and solubility of the ylide.

The promising properties of poly(*para*-phenylenevinylene) (PPVs), such as high conductivity, large nonlinear optical response, light-emitting performance and application on polymer lasers, have spurred the increasing interest in the synthesis of novel PPVs.[1] There are several condensation methods available to prepare PPVs: the Wittig condensation reaction,[2–4] the Wessling route[5] and the Heck coupling reaction.[6] Among these methods, the Wittig reaction is widely used because of its mild conditions and simplicity of handling, and in particular due to its versatility for tailoring the structure and properties of the resulting PPVs.

A typical Wittig polycondensation involving a bis(triphenylphosphonium) salt yielded a mixture of *cis*/*trans*-olefin geometries and the low molecular weight products. However, the presences of *cis* isomers and low molecular weight products are detrimental to the emission properties and PLED performance.[2–4] To synthesize highly *trans*-enriched and high-molecular weight PPVs remains one of the greatest challenges facing synthetic chemists.

The stereoselectivity of Wittig reaction[7–10] is dependent on several factors, such as the nature of the substituents on the phosphorus atom of the ylide, the ylidic carbon, the carbonyl group and the reaction conditions, such as the nature of the base utilized, solvent polarity, concentration and temperature. The preference for *cis* isomers that result in the typical Wittig reaction is presumed to originate from the presence of the phenyl groups on the ylidic phosphorus atom. Therefore, modifying the substituents on the phosphorus atom would play an important role on the stereoselectivity of the Wittig reaction.[8] There are a few reports, which have demonstrated that the replacement of the bulky phenyl groups on the phosphorus atom by alkyl groups dramatically increased the proportion of *trans*-olefin and the activity of ylide.[11–13] However, to the best of our knowledge, these investigations have only confined themselves to small alkenes. There are no further studies on polymers. This study details the first example in which high-*trans* PPVs was synthesized by using a tributylphosphorus ylide instead of the bulkier triphenylphosphorus ylide.

The modified Wittig polycondensation is outlined in Scheme 1. For comparison, the typical Wittig and Wittig–Horner[14] reaction are also depicted according to reported procedures. Like the triphenylphosphonium salt, the tributylphosphonium salt was easy to prepare in good yield by refluxing bis(chloromethyl) benzene with tributylphosphine in DMF. Because of its excellent solubility in chloroform, the tributylphosphorus ylide could be condensed with a dialdehyde in dried chloroform in the presence of sodium ethoxide solution catalyst (0.8 M in absolute ethanol) at room temperature. However, for the triphenylphosphorus ylide, a much

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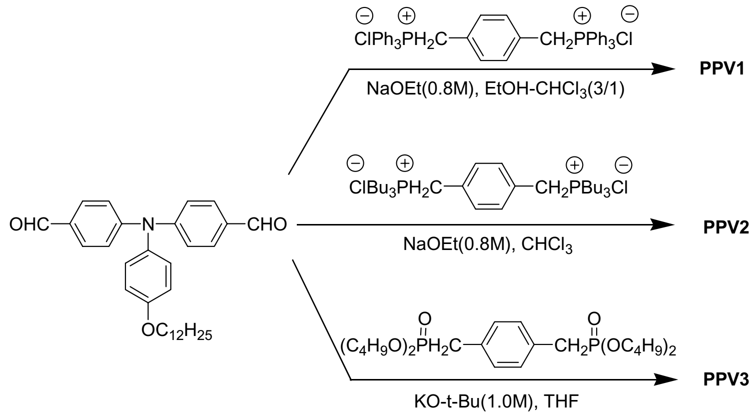


**Scheme 1.** The Wittig, modified Wittig and Wittig–Horner reactions.

**Table 1.** Polymerization results and properties of polymers

| Polymer | Yield (%) | *trans*[a] | $M_w$ | $M_n$ | $T_g$ (°C) | $\lambda_{abs}$ (nm)[b] | $\lambda_{onset}$ (nm)[b] | $\lambda_{PL}$ (nm)[b] |
|---|---|---|---|---|---|---|---|---|
| PPV1 | 70 | 60% | 9000 | 6200 | 89 | 416 | 478 | 498 |
| PPV2 | 79 | 98% | 89,400 | 41,000 | 150 | 434 | 485 | 503 |
| PPV3 | 40 | 100% | 44,600 | 23,000 | 170 | 434 | 485 | 503 |

[a] Determined from dividing the integration of the peaks at $\delta = 6.5$ ppm by that at $\delta = 3.9$ ppm.

[b] Performed in dilute THF solution ($5\times10^{-6}$ M).

more polar solvents, such as ethanol/chloroform was required to perform the homogeneous polymerization. The results of the different polymerizations are listed in Table 1.

The structures of PPVs obtained by these different methods were characterized by $^1$H NMR and FT-IR spectra. PPV1 synthesized by the typical Wittig reaction displayed a complicated $^1$H NMR spectrum, in which a significant resonance at $\delta$ 6.5 ppm could be assigned to *cis*-stilbene moieties. As a result of its low molecular weight, PPV1 also exhibited the peaks of remaining unreacted aldehyde groups. In contrast, the spectrum of PPV2 indicated that no signals due to unreacted groups, and the intensity of peak at $\delta$ 6.5 ppm was dramatically decreased. Moreover, it was identical to the spectrum of all-*trans* PPV3,[15] suggesting that the *trans*-selectivity of the modified Wittig reaction was greatly improved. The *trans* percentage of PPV1 was estimated to be 60% as determined by dividing the integration of the peaks at $\delta$ 6.5 ppm by that at $\delta$ 3.9 ppm (assigned to the –OCH$_2$– of the side chain on the triphenylamine moiety). However, the percentage of *trans*-isomer in PPV2 was increased to 98% due to the modification of the Wittig reaction. This conclusion was also supported by the FT-IR spectra of the polymers (Fig. 1).

PPV2 displayed a similar IR absorption behavior to that of all-*trans* PPV3 with a strong *trans*-vinylene C–H out-of-plane absorption located at 958 cm$^{-1}$ and with no evident peak at approx. 696 cm$^{-1}$ corresponding to the *cis*-vinylene C–H out-of-plane absorption.[16] However, there are much stronger absorptions due to the *cis*-isomer moieties and the remained aldehyde groups in the FT-IR spectrum of PPV1.

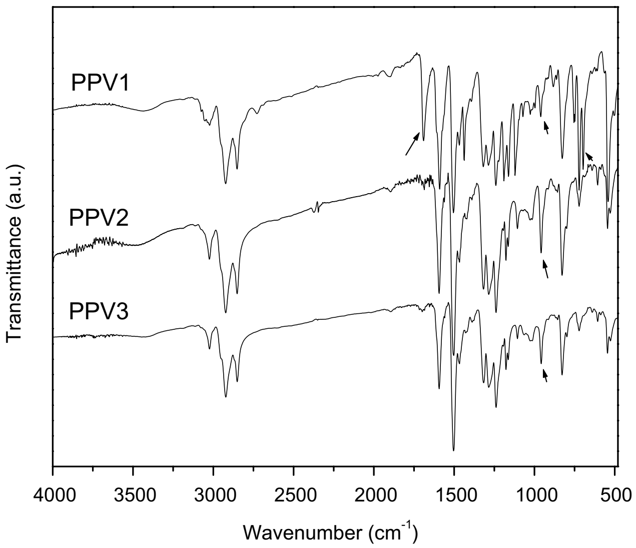
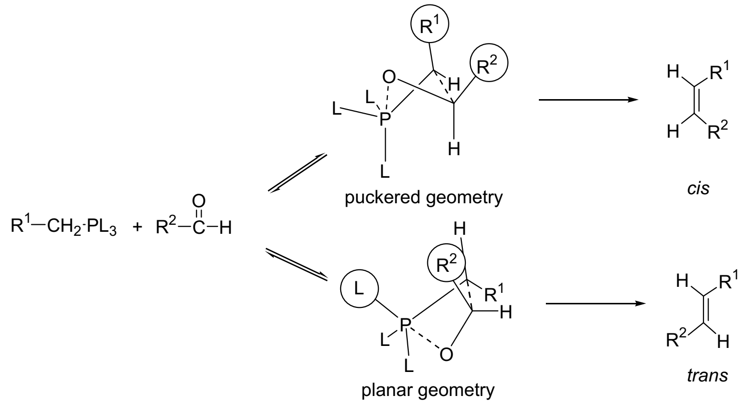


**Figure 1.** FT-IR spectra of PPV1-3.

Vedejs and Marth has proposed that the formation of oxaphosphetane and the interplay of 1,2-steric interactions between R$^1$ in the ylide and R$^2$ of the aldehyde, and the 1,3-interaction between R$^2$ and the substituent L on the phosphorus atom in the four-centre transition states ('puckered' or 'planar' geometry) are responsible for kinetic *cis*- or *trans*-selectivity of the Wittig reaction (Scheme 2)[8]. In the case of the typical Wittig reaction, the 1,2-interaction between the bulky R$^1$ (benzylic group in ylide) and R$^2$ (diarylaminophenyl group in aldehyde) favoured the planar geometry, but the existence of 1,3-interaction between R$^2$ and phenyl of the phosphine



**Scheme 2.** Stereochemistry of Wittig reaction.

made this reaction to be less stereoselective (60% *trans*). By replacing the more bulky phenyl rings with butyl groups, the steric interactions between $R^2$ (triphenylamine) and L (butyl) on the phosphorus atom are decreased. Thus, the *trans*-selectivity of the modified Wittig reaction was largely enhanced (98%) due to the 1,2-steric interactions between $R^1$ and $R^2$. As well, the less polar solvent might also plays a certain role on the *trans*-selectivity. [9]

For the typical Wittig polymerization, the polar solvent not only inhibits the formation of *trans*-isomer, but also leads to precipitation of the resulting low molecular weight polymers and thus prevents their further growth.[17] By modifying with butyl groups, the tributylphosphonium salt is fully soluble in chloroform. As a result, the modified Wittig polymerization could be performed in chloroform and the resulting polymers can continue to grow further, without precipitation. The molecular weights of the polymers formed were determined by gel permeation chromatography (GPC), listed in Table 1. The weight-average ($M_w$) and number-average ($M_n$) molecular weight of PPV2 were approximately 89,400 and 41,000, respectively. The typical degree of polymerization was around 70, which is 10-fold higher than that of PPV1. The improvement of molecular weights of PPV2 is also believed to benefit partly from the enhancement of ylide activity originated from the electro-donating butyl groups on the phosphorus atom.[7,9]

Differential scanning calorimetry (DSC) demonstrated that PPV2 possessed a higher glass-transition temperature ($T_g$) of 150 °C as compared to that of PPV1. The enhanced thermal stability, which will benefit the performance of PLED, was ascribed to the high-*trans* conjugated backbone of PPVs.[4] This conclusion was supported by the fact that the all-*trans* PPV3 shows the highest $T_g$ (Table 1).

The UV–vis absorption and photoluminescence (PL) spectra of polymers obtained from the corresponding dilute THF solution are shown in Figure 2. PPV1 displayed a maximum absorption at 416 nm with onset absorption of 478 nm. However, PPV2 possessed a red-shift $\lambda_{abs}$ at 434 nm with an onset of 485 nm, which is exactly identical to that of all-*trans* PPV3. Similarly, the PL spectra also demonstrated that emission of PPV2 was red-shifted about 5 nm ($\lambda_{PL} = 503$ nm) compared with that of PPV1. Moreover, under the same concentration (ca. $5\times10^{-6}$ M) and experimental conditions, much stronger emission was observed in PPV2 and PPV3. The above results suggested that the *trans*/*cis* ratio of PPV2 was dramatically increased, which in turn benefited the higher emission efficiency of PPV.

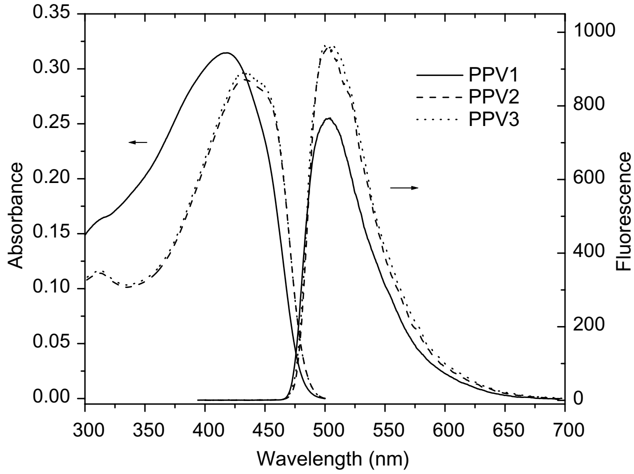


**Figure 2.** UV–vis absorption and PL spectra of PPV1-3 in dilute THF solution ($5\times10^{-6}$ M).

In summary, by replacing the bulky triphenyl rings with tributyl groups on phosphorus atom of ylide, a modified Wittig polycondensation has been developed. This modification allows for a novel and convenient method to prepare high-*trans* and high-molecular weight PPVs.

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