

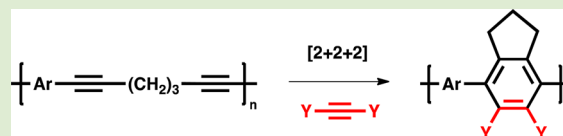
Poly(*para*-arylene)s via [2+2+2]

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Supporting Information

ABSTRACT: We report a versatile new synthetic route to poly(*para*-phenylene)s (PPPs) and related poly(*para*-arylene)s containing high degrees of substitution not readily available by other methods. Our method transforms highly soluble, alkyne-containing polymers into PPPs via high-yielding, transition metal-mediated [2+2+2] cyclizations.



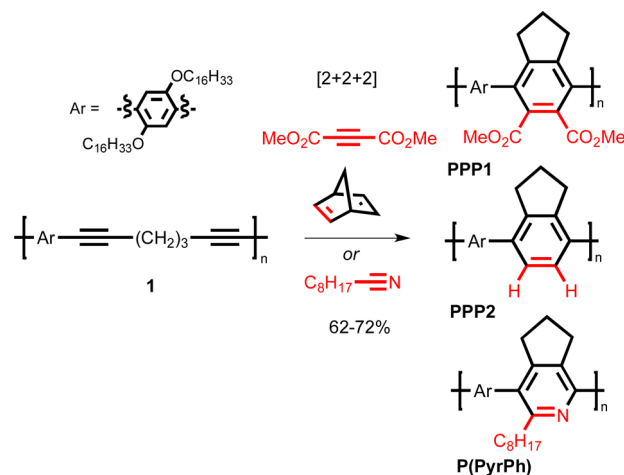
Poly(*para*-phenylene)s (PPPs) are one of the most important semiconductive polymer structures with backbones comprised exclusively of phenylene groups. As a result of this centrality, these materials have received constant investigation for many years.¹ Particular interest in this class of polymers arises from their high thermal and oxidative stability and their use as tunable blue-emitting material for organic light emitting devices (OLEDs).^{2,3}

There are multiple established synthetic strategies to PPPs and related polyarylenes.⁴ However, there are limitations of these different methods, particularly with regard to the creation of functional high molecular weight and soluble PPP materials. Transition metal catalyzed cross-coupling of 1,4-functionalized phenyl groups was one of the most prominent strategies for accessing PPPs.⁴ The coupling of phenyl groups lacking solubilizing side-chains by this method is limited to six repeat units.⁵ Solubilizing substituents dramatically increase the length of PPPs that can be synthesized;⁶ however, the polymerization rates are attenuated by the increased steric bulk. In addition, even with two substituents per phenyl group, these rigid rod polymers still exhibit limited solubility.^{2,6,7} The synthesis of unsubstituted PPPs via the aromatization of soluble precursor polymers is the preferred route to this parent material.^{1b,8,9} Although this strategy has resulted in considerably higher molecular weight polymers by circumventing insolubility issues, the resulting polymers can still possess structural irregularities resulting from incomplete aromatization.⁴ Another synthetic strategy for accessing PPPs is the oxidative coupling of aryl monomers. The harsh conditions used in this process are less favorable, and only low molecular weight oligomers are typically possible from these methods, regardless of solubilizing substituents.^{4,9}

The substituents attached to PPP play an integral role in the polymer properties and can determine their intra- and interchain interactions.^{7b} The most readily accessible 3,5-substitution pattern along the PPP backbone generates a regular structure that can promote interchain associations that affect the solubility of the polymer.⁴ The phenyl–phenyl junctions are sensitive to the steric interactions induced by the substituents, and thus substituted PPPs have twisted, nonplanar conformations and absorption and emission spectra that are blue-shifted relative to unsubstituted analogues.¹⁰

In considering new synthetic strategies for polyarylenes, we decided to take a post-polymerization functionalization approach. This has the advantage that we could choose a polymerization that is known to provide access to higher molecular weight materials and then convert it to the final polymer. To accomplish this we selected the transition metal-mediated [2+2+2] reaction as a method capable of generating a polyarene with few defects. An added bonus of this approach is that [2+2+2] reactions are a proven method for efficiently forming dense substitution patterns in aromatic systems.¹¹ Additionally, by utilizing nitriles as one of the constituent elements,¹¹ *N*-heterocyclic analogues are readily accessible from a single precursor polymer (Scheme 1). In total the combination of highly soluble starting polymers, **1**, and the wide range of viable acetylene partners offers an exciting new route to various poly(*para*-arylene)s.

The success of this method requires a solubilizing phenylene group to be included in Polymer **1**. Previously, end-capped

Scheme 1. Synthesis of Poly(*para*-arylene)s via [2+2+2] with Various Acetylenes or Nonanenitrile

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oligomers of Polymer **1** had been synthesized using traditional Sonogashira-polymerization methods.¹² Thus, with a slight excess of 1,6-heptadiyne and 1,4-bis(hexadecyloxy)-2,5-diiodobenzene, we were able to isolate polymer **1** with a suitably high molecular weight for our studies ($M_n = 20.5$ k, PDI = 1.8, DP \approx 32). However, considering that Sonogashira polymerizations performed between aryl comonomers can produce much higher molecular weights,¹³ we are confident that related structures of higher molecular weight analogues of **1** could be synthesized.

PPP1 and **PPP2** were isolated in moderate yield after the reaction of Polymer **1** with dimethylacetylenedicarboxylate (DMAD) and norbornadiene, respectively, using Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$.¹⁴ Accessing pyridine-containing compounds via [2+2+2] reactions using nitriles not activated with electron-withdrawing groups has been a challenging task relative to the phenyl-containing analogues.¹¹ Gratifyingly, we were able to achieve the desired transformation using nonanenitrile with a catalytic system comprised of hexahydrate cobalt(II) chloride, zinc, and 1,2-bis(diphenylphosphino)ethane.¹⁵ These reactions were initially performed under argon atmosphere at 100 °C, in PhMe (16 h), and the resulting polymers, **PPP1**, **PPP2** and **P(PyrPh)**, were analyzed by NMR, gel permeation chromatography (GPC), infrared (IR), and ultraviolet–visible (UV–vis) spectroscopy to determine the efficiency of the [2+2+2] reaction as a post-polymerization functionalization reaction. Upon analysis of data from these conditions, it was evident that the desired transformation occurred but yet apparent that alkyne functionality was still present within the polymers. This result reflects the challenge of synthesizing homogeneous polyarylenes by post-polymerization reactions, wherein quantitative yields are required.¹²

We hypothesized that the incomplete conversion was the result of the poor solubility of our product polyarene in these reaction conditions. Thus, we turned to conditions wherein the reaction could be heated rapidly to higher temperatures to circumvent competitive aggregation/precipitation. Our optimized reaction reactions were therefore performed with microwave heating (1 h, 150 °C, in PhMe). No solid precipitate was observed in the crude mixture when microwave conditions were employed. The resulting isolated polymers displayed a complete loss of detectable alkyne groups as determined by IR spectroscopy and ¹³C NMR. As expected, the products have limited solubility in typical organic solvents, presumably as a result of their rigid-rod backbone structures.

The ¹H NMR spectra of **PPP1**, **PPP2**, and **P(PyrPh)** (Supporting Information, Figures S.3, S.5, S.7) are best compared directly with Polymer **1** as shown for **PPP1** in Figure 1. Although the ¹H NMR data alone are insufficient evidence for the complete conversion of **1** to a polyarene, it crucially shows the incorporation of key elements. Polymer **1** is more flexible and therefore has a sharper ¹H NMR spectrum than **PPP1**. As indicated in Figure 1, the methylenes between the alkynes shift and a new methyl ester signal is observed.

IR spectra of the product polyarenes proved to be the most convenient method for discerning the extent of conversion of the alkyne groups from Polymer **1** into aryl groups. Additionally, the incorporation of any further functional groups can be easily monitored this way. Representative IR spectra of the optimized process are shown in Figure 2.

We also considered that cross-linking reactions between alkynes in different polymer chains could yield defects in the final structures. However, it appears that we successfully

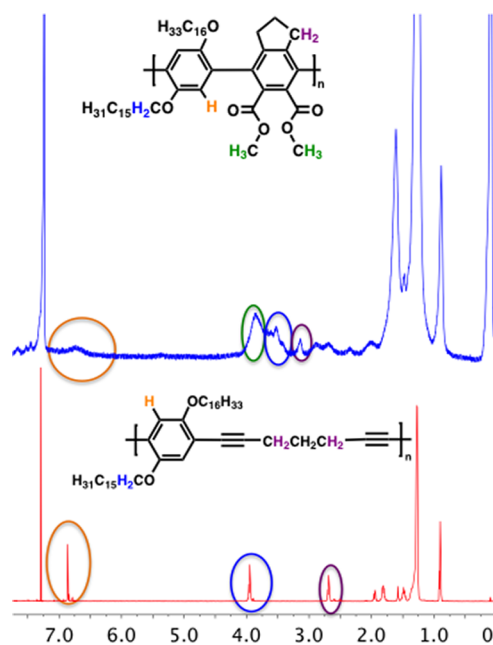


Figure 1. ¹H NMR spectra of Polymer **1** before (red) and after (blue) [2+2+2] reaction with DMAD (**PPP1**). Key functional groups and their resonances are indicated for clarity.

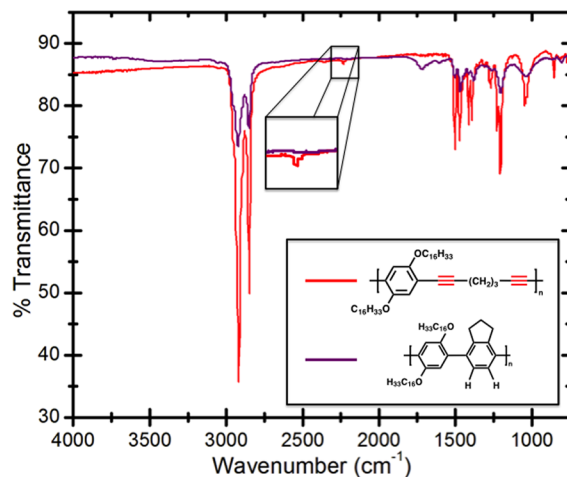


Figure 2. IR spectra of Polymer **1** (red) and **PPP2** (purple).

negated cross-linked product formation by employing an excess of the DMAD, norbornadiene, or nonanenitrile partner during our reactions. As determined by GPC, the polymers before and after the [2+2+2] display a monomodal chromatogram with little change in the apparent molecular weight. Cross-linked material would have produced a considerably higher mass and a distorted GPC trace of the final polymers (Figure 3).

The conjugation length in poly(*para*-arylene)s is directly correlated to the dihedral twist between adjacent aryl groups. This twist is modulated by the steric interactions of the respective substituents.⁴ As a result, the different acetylenic partners in our [2+2+2] reaction should result in varying optical band gaps in the product polymers. These differences are revealed in the UV–vis absorption spectroscopy (Figure 4). The minor differences in the absorption onset at long wavelengths of the product polymers suggest that the interactions between the fused five-membered rings and the ethers on adjacent arylenes are the dominant steric interactions.

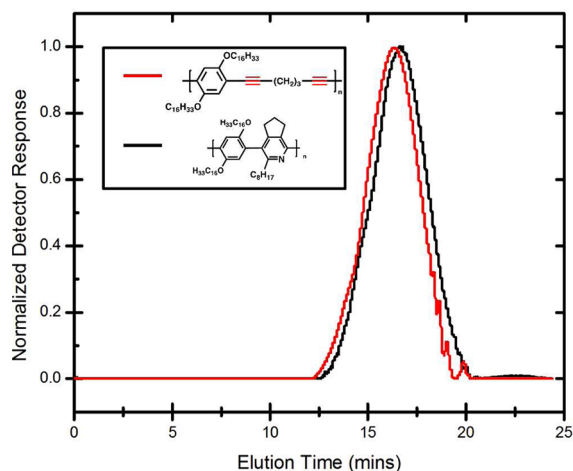


Figure 3. THF GPC traces (UV detection 254 nm) of starting Polymer 1 (red) and P(PyrPh) (black).

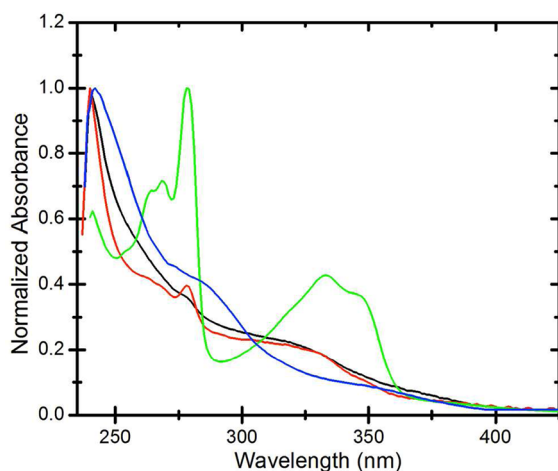


Figure 4. Comparison of the UV-vis spectra for Polymer 1 (green), PPP1 (black), PPP2 (red), and P(PyrPh) (blue).

This can be deciphered specifically in the band gap of PPP2, which lacks the ester or hydrocarbon substituents of PPP1 or P(PyrPh), respectively, but still possesses a similar absorption spectrum. Comparisons of the absorption spectra can also be used as a crude estimate of extent of conversion as previously shown for oligomers of Polymer 1.¹⁶ Product polymers that possess a low degree of conversion from Polymer 1 have been seen to maintain absorption features of the starting polymer, once more suggesting that we have achieved a high degree of post-polymerization conversion.^{16,17}

In conclusion, we have demonstrated the viability of the metal-mediated [2+2+2] reaction to efficiently furnish minimally defective, high-molecular weight poly(*para*-arylene)s starting from readily accessible, highly soluble polymers. In demonstration of potential versatility of this strategy, we prepared two different poly(*para*-phenylene)s and a poly(*para*-pyridylene). We found the use of a microwave critical in obtaining high-quality PPPs. Further studies to extend the application of this strategy to other polymers is now underway in our lab.

■ ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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