Synthesis of poly(*para*-phenylene)(2-isocyano-2-tosylpropane-1,3-diyl), poly(*para*-phenylene)(2-oxopropane-1,3-diyl) and oligo(cyclopentadienones) *via* carbonylative coupling of α,α′-dibromoxylene†

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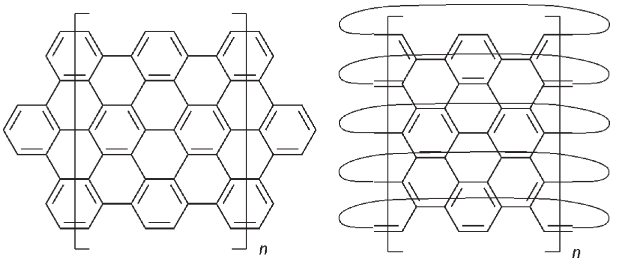
Poly(*para*-phenylene)(2-oxopropane-1,3-diyl), a potential precursor of linear graphene, is generated in low yield from hydrolysis of a previously unknown poly(*para*-phenylene)-(2-isocyano-2-tosylpropane-1,3-diyl) generated from inexpensive, commercially available starting materials.

Linear[1] and cyclic[2] fused polyaromatic hydrocarbons have been synthesized by many groups, and are of increasing importance due to their processability, relatively low expense, and low band gaps. Oligomeric and polymeric graphitic materials[3] and nanotubes[4] have been investigated; however no synthesis of a monodisperse carbon nanotube or a purely linear, oligomeric graphene has been reported to date.‡ These materials are of great interest for their potential as components for photovoltaic cells, components of nanoscale field effect transistors,[5] and as shape persistent structures for supermolecular assemblies.[6]



More recently[7] polymers consisting of tetraarylcyclopentadienone units have been suggested as low band gap semiconductors and possible superconductors due to the low calculated HOMO–LUMO gap of the monomer (*ca.* 2.72 eV) and the subsequent reduction in band gap after polymerization which arises from the increase in the extent of conjugation.

Due to our interest in polyaromatic macrocycles and polymers we have decided to pursue the synthesis of oligo(*para*-phenylene)(2-oxopropane-1,3-diyl) for later conversion to oligocyclopentadienones and ultimately to oligohexaarylphenylenes, both as macrocycles for the synthesis of carbon nanobelts and as linear oligomers for the products of graphitic ribbons.

Carbonylative couplings with $Na_2Fe(CO)_4$ have been conducted in our laboratories to provide symmetrical and asymmetrical heterosubstituted diphenylacetones in high yield.[8] However, when the aromatic rings are substituted with electron withdrawing groups, the yields are significantly lower. We have now found that the van Leusen[9] TOSMIC reaction is capable of producing these electron poor dibenzyl ketones in moderate yields that are at least as good as those reported in the literature[10] (Fig. 1). van Leusen couplings have also been conducted asymmetrically,[9] but this has not yet been pursued by our group.

(*para*-Phenylene)(2-oxopropane-1,3-diyl) macrocycles have been reported previously by Sasaki and Kitagawa[11] using a van Leusen carbonylative coupling reaction at high dilution. We have reproduced these results, and have successfully purified and characterized the cyclic trimer, tetramer and pentamer. It was reasoned that performing this reaction, or the Collman coupling, at higher concentrations would lead to linear oligomers. Concentration of the TOSMIC coupling conditions does produce the previously unreported polymer poly(*para*-phenylene)(2-isocyano-2-tosylpropane-1,3-diyl) (**PPIT**) (Fig. 2).

Alternatively, the reaction of α,α′-dibromoxylene with $Na_2Fe(CO)_4$ at high dilution led to a complex mixture of products which did not contain a significant amount of macrocycle of any degree of polymerization, presumably due to the slow rate-determining second alkylation required for the ring closure step.[8,12] This reaction was not run under more concentrated conditions to obtain linear polymer because the kinetics would still be disfavorable, and because of the success encountered using the TOSMIC reagent.

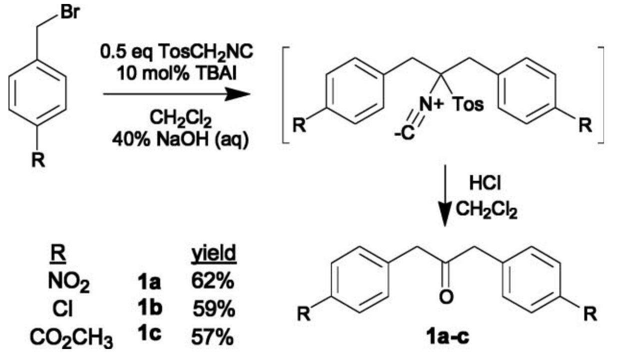


Fig. 1 van Leusen coupling of benzyl bromides.

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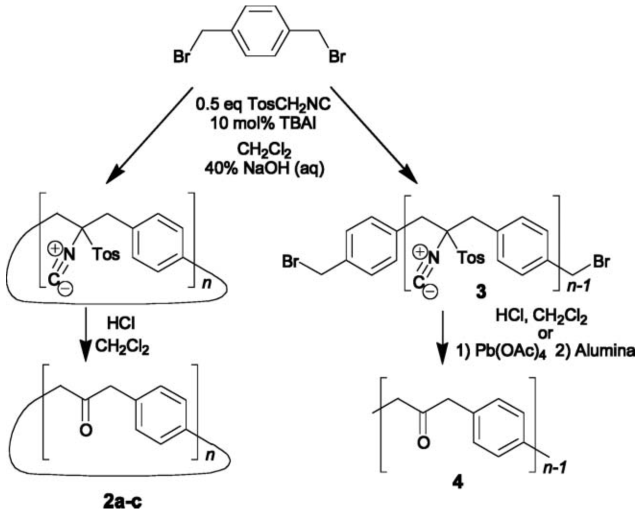

Fig. 2 Tosylmethyl isocyanide mediated polymerization.

Employing the TOSMIC reagent in a biphasic reaction mixture using TBAI as the phase transfer catalyst and aqueous sodium hydroxide as the base, polymer **3** was obtained. GPC showed a reproducible X_n of 24–25, corresponding to an M_n of 9600. The polydispersivity was measured to be 1.37, and was reproducible from batch to batch. ^1H NMR (Fig. 3) end-group analysis comparing the integrations of the diastereotopic benzylic protons to that of the remaining benzyl bromide groups gave an X_n of 30.5. The reaction can be conducted easily on a multigram scale, but decomposition of the polymer occurs slowly at room temperature, requiring refrigeration if storage for longer than a few weeks is necessary.

Due to the reactivity of the pendant functional groups we believe this polymer could prove useful for further functionalization to novel polymers. Methodology developed by other groups[13] allows the potential for the conversion of **PPIT** to poly(*para*-phenylene)(propane-1,3-diyl), polyisocyanide and polyisocyanate polymers.

Hydrolysis of **PPIT 3** affords the corresponding poly(*para*-phenylene)(2-oxopropane-1,3-diyl), **4** (Fig. 4). The hydrolysis of macrocycles **2** with HCl in methylene chloride is straightforward, but the hydrolysis of polymer **4** is less well-behaved. Higher concentrations of acid lead to product mixtures of low solubility and poor conversion. However, hydrolysis with dilute HCl gives much higher conversion to the ketone functionality. Alternatively, the isonitrile can be converted to the isocyanate with lead tetraacetate; this polyisocyanate is easily hydrolyzed to **4** upon stirring with alumina in methylene chloride. This method gives lower conversion to the ketone, but suggests further chemical transformations of **3**, which are currently being pursued in our laboratories.

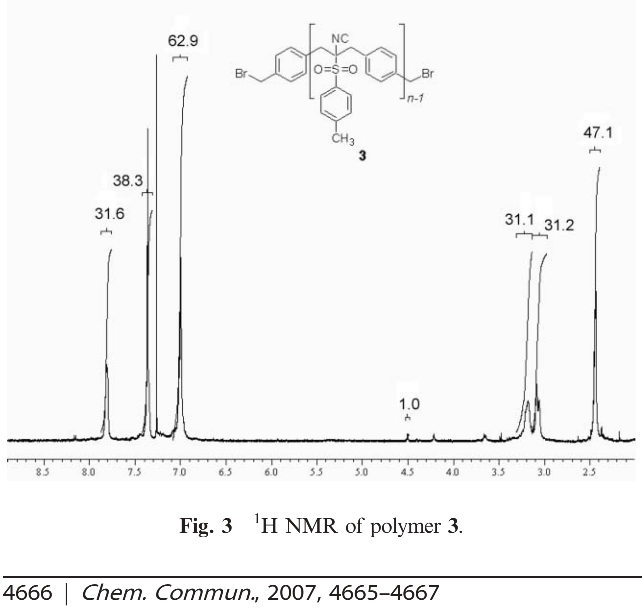

Fig. 3 ^1H NMR of polymer **3**.

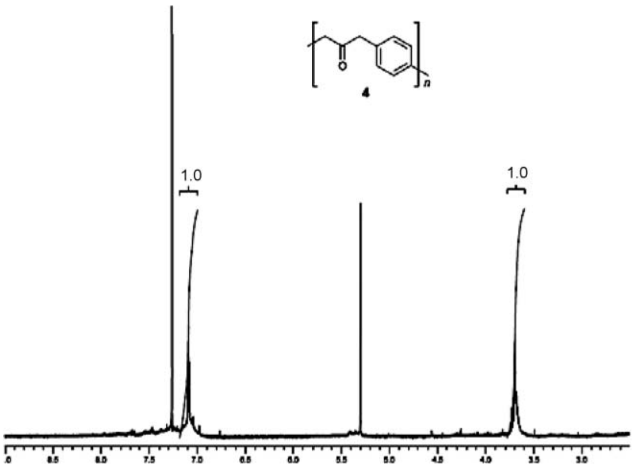

Fig. 4 ^1H NMR of polymer **4**.

To determine the feasibility of synthesizing a tetraphenylcyclopentadienone polymer that would require multiple Knovenagel condensations on the 1,3-diphenyl-2-propanone moieties in **4**, the multiple Knovenagel condensation was attempted on shorter oligomers which were prepared by performing the polymerization with an excess of monofunctional reagent. By employing a 2 : 1 stoichiometry of benzyl bromide to α,α′-dibromoxylene in the TOSMIC carbonylative coupling reaction, diketone **5a** and triketone **5b** oligomers can be isolated in low yields, as shown in Fig. 5. The unoptimized yields are low, but it should be noted that the hydrolysis of these short oligomers is quite facile without any problems of solubility, a result similar to that observed for small cyclic oligomers but not for the polymer.

Initial Knovenagel condensations performed on diketone **5a** (and tri-ketone macrocycle) using potassium hydroxide in ethanol led to complete decomposition of the dark purple reaction mixture upon exposure to the atmosphere. Mass spectrometry of the complex product mixture contains peaks consistent with

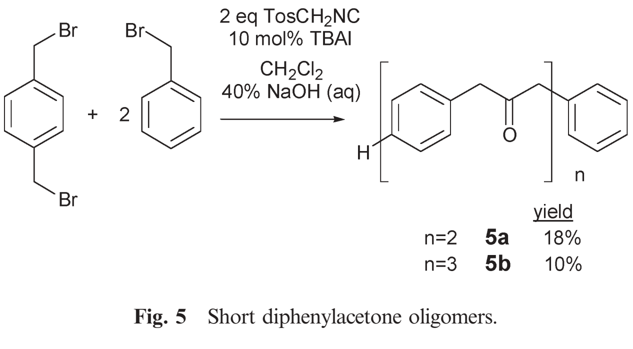

Fig. 5 Short diphenylacetone oligomers.

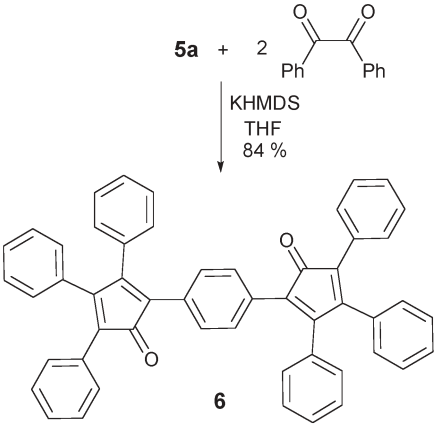

Fig. 6 Synthesis of tetraphenylcyclopentadienone dimer.

photo-oxidation products.[14] After exclusion of light and oxygen prior to low temperature aqueous workup, condensation of **5a** with benzil led to a low yield of the corresponding tetraphenylcyclone **6** (Fig. 6). However, the majority of the product mixture was composed of a variety of regioisomers and diastereomers resulting from hydration of the four cyclopentadienone double bonds of **6**. Once purified, **6** and its hydrates are as stable (for several months after removal of solvent) as substituted monomeric tetraarylcyclopentadienones.

To avoid the production of the hydrate products, potassium bis(trimethylsilyl)amide in a solution of THF was employed. These reaction conditions led to an 84% yield of **6**, and no apparent hydrate or photooxidation side products. The apparent increase in reactivity of the intermediates leading to **6**, or of the product itself, was originally thought to be attributable to the lowering of the LUMO arising from the increased conjugation. However, a B3LYP/6-31G(d) computation reveals a HOMO–LUMO gap similar to those of other electron-rich tetraarylcyclopentadienones synthesized in our laboratory with no such sensitivity to oxygen and a LUMO comparable to that in parent tetraphenylcyclopentadienone which is not so susceptible to nucleophilic attack that it cannot be prepared using hydroxide base. It should be noted that the yield obtained in this multiple Knovenagel condensation is much higher than those reported for the synthesis of other bis(tetraphenylcyclopentadienone) isomers using hydroxide bases where strict removal of oxygen and light was not performed.[15] Initial attempts to convert oligomer **5b** to a trimeric cyclopentadienone were not successful, which we attribute to the small scale of those reactions and the possibility that the linear trimer **5b** may be long enough to undergo back-biting aldol condensations with itself that are not possible for shorter **5a**.

Due to the low cost of the starting materials and the ease of the experimental conditions we believe even a low yielding conversion of the cyclic or linear oligomers to polycyclopentadienones to be a potential pathway to linear and cyclic tetraarylcyclopentadienone oligomers, as well as polymers. We also believe the **PPIT** polymer to be a useful precursor for the production of a variety of functionalized low molecular weight polymers which may not be accessible through current methology.

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‡ Although non-discrete examples are numerous, see refs. 1 and 2.

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