

Communications to the Editor

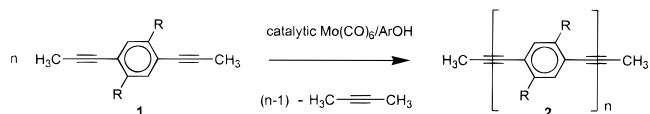
Alkyne Metathesis with Simple Catalyst Systems: Poly(*p*-phenyleneethynylene)s

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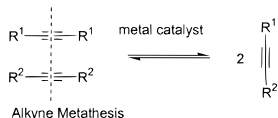
Received April 23, 1998

We describe in this communication conditions under which an in situ catalyst system (molybdenum hexacarbonyl and *p*-(trifluoromethyl)phenol) efficiently metathesizes 1,4-dipropynylbenzenes (**1**) to poly(*p*-phenyleneethynylene)s (PPE, **2**), at-



tractive materials for photonic devices such as LEDs and polymer-based lasers.¹

Alkyne metathesis is now an established and powerful tool for organic, bioorganic,² and polymer synthesis.^{3,4} The conceptually



related process of alkyne metathesis, however, has found much less attention. Metathesis of C–C triple bonds by molybdenum/phenol species has been known since the 1970s⁵ but was never developed into an established synthetic method. A recent report describes the metathesis of internal alkynes at elevated temperatures, utilizing a Mo(CO)₆/*p*-chlorophenol mixture.⁶ The yields did not exceed 80%, even if one component was added in large excess or removed to drive the cross metathesis to completion.

The well-defined tungsten alkylidydes, introduced by Schrock,⁷ are active for alkyne metathesis. Scattered examples are known

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where (*t*BuO)₃W≡C*t*Bu (**3**), a superb catalyst, has been used to generate polymers by ring-opening of strained cyclic alkynes.^{8,9}

We have used **3** for ADIMET (acyclic diyne metathesis) of dipropynylated benzenes (**1**) to form high molecular weight PPEs (**2**).¹⁰ Although high molecular weight PPEs have been obtained by the Pd-route in some cases,¹¹ ADIMET circumvented the problems associated with the classic Pd-catalyzed couplings, difficult separation of phosphorus and palladium containing catalyst residues, ambiguity regarding the end groups (dehalogenation, formation of phosphonium salts),¹² and the occurrence of defect structures (butadiyne linkages formed by oxidative coupling of terminal alkynes).¹³ The preparation of pyrophoric **3**, however, is difficult and requires rigorous exclusion of air and moisture. It can only be handled safely in an inert atmosphere. These considerations render the ADIMET reaction utilizing **3** less attractive. We therefore set out to develop an alternative, simple ADIMET route to PPEs.

Despite the moderate yield, we decided to attempt the transformation of dipropynyl benzenes (**1**)^{14,15} into PPEs, using the easily accessible Mo(CO)₆/phenol system. For polymer formation, **1a** (R = hexyl) was reacted in 1,2-dichlorobenzene with a molybdenum hexacarbonyl/*p*-(trifluoromethyl)phenol combination as catalyst, (see Table 1 entry 2) for 16 h at 150 °C. From prior experiments, we knew that *p*-(trifluoromethyl)phenol was more active as cocatalyst than *p*-chlorophenol (entry 1). An important experimental detail is that the byproduct butyne always had to be removed by a constant N₂ purge.¹⁶ No attempts were made to dry or exclude O₂ from the reaction mixture. Workup

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(14) A series of substituted diiodobenzenes **5a–h** was synthesized according to literature procedures described in ref 13b and propynylated to give the monomers **1a–h**.¹⁵

(15) (a) In a 500-mL round-bottomed flask, closed with a ground glass valve and evacuated to 1 mmHg were placed 4.98 g (10.0 mmol) of **5a**, piperidine (50 mL), PdCl₂(PPh₃)₂ (351 mg, 0.500 mmol), and CuI (190 mg, 1.00 mmol). Propyne (520 mL, 760 mmHg) was added through the valve. The closed flask was shaken for 4 h. Aqueous workup, chromatography (silica gel, hexanes), and crystallization from ethanol yielded 2.65 g (82%) of **1a**. The other dipropynyls **1** were produced accordingly. (b) The optically active **1e** was obtained from commercially available (*S*)-(+)-citronellyl bromide after catalytic hydrogenation (no loss of the bromine functionality), transformation into its Grignard reagent and coupling to 1,4-dichlorobenzene under standard Kumada¹⁷ conditions. Iodination¹⁴ and propynylation yields optically active **1e**. (c) Structural proof was obtained by solid-state ¹³C NMR spectroscopy, which showed the three expected signals for the arene ring, one resonance for the alkyne group, and the expected four features for the solubilizing *iso*-pentyl groups.

Table 1. Results of the ADIMET-Polymerization of Dipropynyl Benzenes **1** Utilizing Mo(CO)₆/ArOH Catalyst Systems

entry	substituent 1,2	polymerization condition	ArOH 50 mol %	yield PPE 2	P _n NMR	P _n GPC	M _w /M _n GPC	λ _{max} 2 nm
1	a hexyl	125 °C, 16 h, 5 mol % Mo(CO) ₆	4-Cl-phenol	85 %	59			404
2	a hexyl	150 °C, 16 h, 5 mol % Mo(CO) ₆	4-CF ₃ -phenol	quantitative	94	150	3.5	396
3	b -CH ₂ CH ₂ CH(CH ₃) ₂	150 °C, 16 h, 5 mol % Mo(CO) ₆	4-CF ₃ -phenol	quantitative			insoluble	382
4	c -CH ₂ CH(CH ₂ CH ₃) ₂	150 °C, 16 h, 5 mol % Mo(CO) ₆	4-CF ₃ -phenol	96 %		50 soluble fraction	3.8 barely soluble	384
5	d -2-(ethyl)hexyl	150 °C, 16 h, 5 mol % Mo(CO) ₆	4-CF ₃ -phenol	93 %		180	2.6	387
6	e -[S-(+)-(CH ₂) ₂ CHMe(CH ₂) ₃ CH(CH ₃) ₂]	150 °C, 16 h, 5 mol % Mo(CO) ₆	4-CF ₃ -phenol	quantitative	>150	500	2.5	396
7	f -OCH ₂ CH ₂ CH(CH ₃) ₂	130 °C, 16 h, 5 mol % Mo(CO) ₆	4-Cl-phenol	25 %	8			275
8	f -OCH ₂ CH ₂ CH(CH ₃) ₂	130 °C, 16 h, 10 mol % Mo(CO) ₆	4-CF ₃ -phenol	quantitative	15	78	2.7	440
9	g -CO ₂ CH ₂ CH ₂ CH(CH ₃) ₂ -CH ₃	130 °C, 16 h, 10 mol % Mo(CO) ₆	4-CF ₃ -phenol				no polymer	

gave rise to the isolation of **2a** in quantitative yield.¹⁶ Soxhlet extraction with boiling chloroform redissolved **2a** completely, regardless of its history. The degree of polymerization (P_n) and purity were obtained from ¹H NMR spectroscopy. The propyne end groups appear as a singlet at δ 2.04, where no other signals of **2a** are observed; thus, a P_n = 94 was estimated by end group integration (see Table 1). We performed gel permeation chromatography (GPC) on this polymer, measuring P_n ≈ 150 and a polydispersity index (M_w/M_n) of 3.5. The disparity of GPC and NMR data is not surprising since it is known that P_n of stiff macromolecules is overestimated by GPC, rendering the NMR data more reliable.

To study the effect of branching with respect to solubility, **1b–d** were prepared. Polymerization afforded the corresponding PPEs **2** (see Table 1). Polymers **2b,c** carrying the 3-methylbutyl and the 2-ethylbutyl substituent, respectively, were completely insoluble.^{15c} 2-Ethylhexyl-substituted **1d** was polymerized to **2d** with considerably increased P_n and solubility. The most impressive result was obtained for ADIMET of optically active **1e**. In **2e**, the end groups no longer could be detected by proton NMR (P_n ≥ 150). GPC shows an apparent P_n of ~500, yet the material readily dissolved in warm chloroform to give a highly viscous solution. All of the described PPEs are yellow (alkyl substituted) or orange (alkoxy substituted, vide infra). As expected, they display an intense purple (solution) or greenish-blue/yellow (solid state) fluorescence.

To explore the scope of the ADIMET reaction, alkoxy- (**1f**) and an ester-substituted monomer (**1g**) were prepared. The ester **1g** was unreactive under different metathesis conditions, but an initial attempt utilizing **1f** (see entry 7, Table 1) was moderately successful, resulting in low-molecular weight oligomers. Em-

ploying more Mo(CO)₆ (10 mol %, entry 8) led to a dramatically improved yield (quantitative) and increased P_n to 15. As a consequence, the presence of ether linkages in **1** is not detrimental to alkyne metathesis but produces polymers **2f** with a lower P_n.

The catalytically active species in these polymerization reactions is probably a Schrock-type carbyne of the structural formula (ArO)₃Mo≡C-R (**4**), accessed by in situ oxidation of Mo(CO)₆ in the presence of phenols. Such an oxophilic species, **4**, would react with an ester group, and its catalytic activity would be attenuated by the presence of any ether linkage or another donating functionality. We observe that behavior in our catalytic system. Experiments to determine the nature of the active species are under way.

In conclusion, we have shown that *the ADIMET reaction can be performed in an experimentally simple setup, utilizing inexpensive and commercially available catalyst precursors without rigid exclusion of air and moisture.* Ease of process and workup should make alkyne metathesis amenable to facile scale-up of industrial-sized preparations. The in situ catalyst is not only highly active but very selective and efficient for the formation of high-molecular weight PPEs in excellent yields. These attributes endow the described catalyst system with the potential to be a powerful tool for the synthesis of attractive conjugated polymers¹ and novel small molecules containing alkyne units.

Acknowledgment. We wish to thank Prof. Haskell Beckham for the recording of the solid-state NMR of **2b** and **c**, Adam Rawlett for GPC measurements of **2a**, **d**, **e**, and **f**, and Prof. Ken Shimizu (USC) for helpful discussions. The work was financed by the University of South Carolina. LK thanks the Deutsche Forschungsgemeinschaft for a postdoctoral stipend.

Supporting Information Available: Experimental details and spectroscopic characterization of **1–2** (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

(16) Polymerization: **1a** (500 mg, 1.55 mmol), Mo(CO)₆ (21 mg, 0.078 mmol), *p*-(trifluoromethyl)phenol (251 mg, 1.55 mmol), and 20 mL 1,2-dichlorobenzene were placed in a 50-mL Schlenk flask, equipped with a reflux condenser. The reaction mixture was heated for 16 h to 150 °C under N₂ purge. Addition of dichloromethane, removal of the phenol by basic extraction, precipitation into methanol, and drying at 0.1 mmHg for 12 h gave 441 mg (>99%) of polymer **2a** as yellow flakes.

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