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Alkyne metathesis with in situ catalysts: W(CO)$_6$ and 4-chlorophenol are efficient in the formation of poly(*para*-phenyleneethynylene)s

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Abstract

Treatment of several alkyl-substituted dipropynylated benzenes in the presence of tungsten hexacarbonyl and 4-chlorophenol at 150°C leads to the formation of poly(*para*-phenyleneethynylene)s (PPEs). The obtained PPEs are of moderate molecular weights but form in good to excellent yields. Dihexyl-, dinonyl-, and didodecyl-PPE have been made by this route. It is the first time that a tungsten-containing in situ catalyst system is reported to be active for alkyne metathesis. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Defined tungsten and molybdenum carbyne complexes perform catalytic alkyne metathesis efficiently and have been used to close rings and produce polymers [1]. Unfortunately most of these catalysts are highly air- and moisture sensitive and have to be made in a multistep synthetic sequence [2]. Alkyne metathesis in homogeneous solution has been known since 1974, when Mortreux treated an unsymmetrical alkyne with a mixture of Mo(CO)$_6$/resorcinol at 160°C and observed the formation of an equilibrium mixture of three (two symmetrical and the starting alkyne) disubstituted acetylenes [3,4]. Later Mori [5] utilized a similar reaction (Mo(CO)$_6$/4-chlorophenol) for the preparation of unsymmetrically substituted alkynes. These molybdenum-based catalyst systems are less active than the defined alkylidynes, but form

in situ from their commercially available constituents at elevated temperatures in off-the-shelf solvents. Increasing the reaction temperature and removing the alkyne with the lower boiling point improved the reaction protocol. These modified Mortreux conditions allow access to high-molecular weight poly(*para*-phenyleneethynylene)s (PPEs **2**) utilizing the in situ molybdenum catalysts.

The in situ method developed by us [6] is the best way to make dialkyl-substituted PPEs. It is interesting to note that all of the hitherto described chemistry based on the instant catalysts utilize molybdenum as the source of the catalytically active species, while in the case of the defined carbyne complexes the tungsten carbyne [2] (*tert*-BuO)$_3$W≡CMe$_3$) plays a prominent role.

In this contribution we show that instant catalysts formed from tungsten hexacarbonyl and 4-chlorophenol are also active in the acyclic diyne metathesis reaction (ADIMET). They furnish PPEs **2** in high yield and with slightly different properties (molecular weight, molecular weight distribution) compared to the polymers obtained with the Mo(CO)$_6$/4-chlorophenol mixture [6].

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2. Results and discussion

In a first experiment we reacted **1a** with 10 mol% $W(CO)_6$ and 4-chlorophenol for 20 h at 150°C under a N_2 purge. Workup of the fluorescent solution furnished a small amount PPE **2a** of low molecular weight. Gel permeation chromatography (GPC) revealed a P_n of 18 and the UV–vis spectrum of **1a** indicated (Table 1) that a mixture of short oligomers must have been formed. This result was encouraging, because it demonstrated that alkyne metathesis should, in
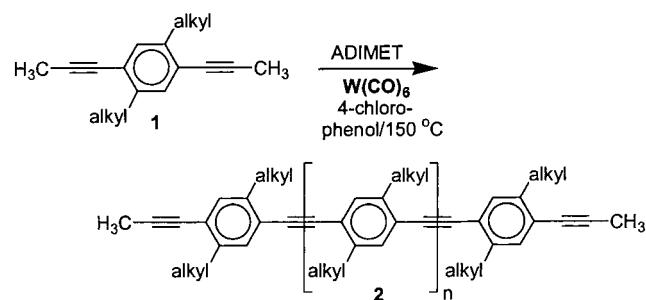
R = **a** Hexyl; **b** dodecyl; **c** ethylhexyl; **d** isopentyl; **e** nonyl

ADIMET: Acyclic Diyne Metathesis

principle, be feasible utilizing tungsten hexacarbonyl–4-chlorophenol mixtures. In a second experiment, the amount of tungsten hexacarbonyl was doubled to 20

mol%. The resulting yield of polymer jumped to 95% and P_n of **2a** increased to 70 repeat units. Repetition of this experiment led to a material of P_n of 52 and a polydispersity of five, suggesting that subtle but unknown changes in experimental conditions lead to polymers **1a** with different polydispersities and molecular weights. A further increase in the amount of tungsten hexacarbonyl did not seem to have a large effect (see Table 1).

With the successful protocol developed for **1a**, we were able to prepare didodecyl (**2b**) and dinonyl PPE (**2e**) in good yields. Under these conditions the P_n values of the PPEs vary between 40 and 160 repeat units, while the polydispersities are generally in the range of $M_w/M_n = 2.6$–6 with some exceptions being higher. Surprisingly, our reaction protocol did not work very well for the synthesis of PPEs with branched 2-ethylhexyl chains **2c**. Here the yields are much lower and only oligomeric material of low molecular weight forms in the course of the reaction. Attempts to polymerize a dipropynyl benzene carrying a trimethylhexyl group, likewise leads only to the isolation of a small amount of low-molecular weight oligomeric material.

The molecular weights in this study were determined by gel permeation chromatography (GPC) versus polystyrene. Due to the fact that PPEs are rigid rods, the absolute values, which we obtain, by GPC, are too high by a factor of approximately 1.5–3. These values

Table 1. See footnote for details [a]

1,2	Substituent	$W(CO)_6$ amount (%)	Time (h)	1 (g)	Yield PPE (%)	P_n (GPC)	$M_n \times (10^{-3})$	M_w/M_n	λ_{max}
a	Hexyl	10	20	0.082	10	18	4.7	1.3	352
a	Hexyl	20	20	0.787	95	71	19	2.6	387
a	Hexyl	20	22	0.805	97	52	14	4.9	382
a	Hexyl	25	21	0.571	76	22	5.9	1.4	374
a	Hexyl	25	22	0.768	92	34	9.2	2.0	381
b	Dodecyl	20	22	1.451	>99	55	24	3.0	378
b	Dodecyl	20	22	1.423	>99	91	40	7.9	380
b	Dodecyl	20	22	1.423	>99	48	21	2.5	375
b	Dodecyl	25	22	1.372	>99	64	28	2.7	377
b	Dodecyl	25	22	1.321	98	135	59	11.0	386
c	Ethylhexyl	20	23.5	0.100	10	17	5.4	1.3	350
c	Ethylhexyl	25	19.5	0.571	57	27	8.6	1.5	369
d	Isopentyl	20	24	0.728	98	38	9.2	1.6	381
d	Isopentyl	25	19.5	0.702	94	50	12	2.3	381
e	Nonyl	20	22	1.076	99	38	14	1.8	378
e	Nonyl	20	19.5	1.078	99	99	35	5.3	387
e	Nonyl	25	20	1.182	>99	160	56	5.5	390
e	Nonyl	25	19.5	0.990	91	117	41	3.1	387

[a] Experimental details, general procedure for the polymerizations. The synthesis and characterization of the monomeric dipropynylbenzenes **1a**–**e** and of the corresponding PPEs **2a**–**e** has been reported. The experimental setup, the instruments used and details for molecular weight determination of the PPEs have been described in detail elsewhere. In a typical reaction, **1** (3.10×10^{-3} mol) and the catalyst system consisting of $W(CO)_6$ (10–25 mol%) and one equivalent of *p*-chlorophenol are dissolved in 20 ml of *o*-dichlorobenzene and stirred at 150°C for 19–24 h removing butyne by a slow stream of nitrogen. The formed fluorescent solution is cooled and any precipitated polymer dissolved by the addition of CH_2Cl_2. The organic layer is washed with 100 ml of each H_2O, 10% NaOH, and 25% HCl. Addition of methanol precipitates the yellow polymer **2**, which is filtered and vacuum-dried. Multiple (34 times) precipitation from methanol leads to material of higher purity. L. Kloppenburg, D. Jones, U.H.F. Bunz, Macromolecules 32 (1999) 4194.

however are sufficient to evaluate relative molecular weights. This is particularly visible when comparing the P_n values obtained from GPC with the recorded λ_{max}. The convergence length of oligo–PEs and PPEs **2** is reached [7] for a 16-mer. It leads to a λ_{max} of approximately 384–388 nm. As a consequence, the GPC values can be cross-checked by absorption. As expected, λ_{max} increases up to an apparent P_n of 50 (GPC), suggesting that the degree of polymerization is overestimated by a factor of three in low molecular weight, rigid rod PPEs.

To expand the scope of this reaction, we attempted to polymerize **1a** in the presence of α,α,α-trifluorocresol, but this phenol does not seem to be capable of activating tungsten hexacarbonyl. Chromium hexacarbonyl or CpRe(CO)$_3$ are likewise both inactive for alkyne metathesis in the presence of activating phenols.

For the first time, we have demonstrated that a mixture of tungsten hexacarbonyl and 4-chlorophenol performs alkyne metathesis successfully and furnishes PPEs **2** with a moderate P_n. Surprisingly, linearly alkyl substituted monomers **1** work much better than derivatives carrying branched alkyl side chains. The reason for this behavior is not understood, but could be a consequence of the increased size of tungsten in comparison to molybdenum, thus leading to a sterically congested catalyst surrounding. The inactivity of trifluorocresol as activating phenol suggests that the tungsten catalyzed reaction is sensitive to changes in reaction conditions. Overall, the tungsten systems are valuable for the synthesis of PPEs **2** with low-to-medium molecular weights. In comparison to our "classic instant" catalysts formed from Mo(CO)$_6$–phenol mixtures, the tungsten-based system is competitive with respect to yield, but furnishes PPEs with a lower P_n. In addition, the tungsten-based systems are only active if the monomers **1** carry linear solubilizing chains. Insofar, these two catalyst systems are complementary to each other, with the molybdenum-based system being over-all more versatile. We are now exploring the functional group tolerance of the tungsten systems and compare them to their molybdenum relatives [6], which are most suited for hydrocarbons and oxygen-containing substrates.

Acknowledgements

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