Palladium-catalysed cycloaddition copolymerisation of diynes with elemental sulfur to poly(thiophene)s

Tetsuo Tsuda*[a] and Atsushi Takeda[b]

[a] *Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan*
[b] *Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan*

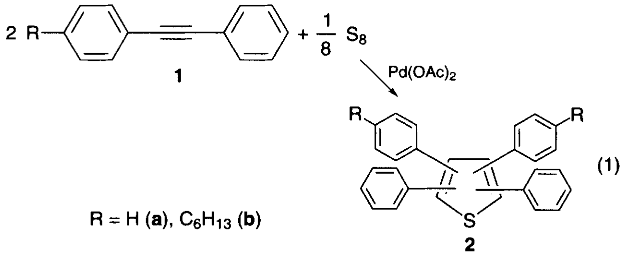
Palladium acetate catalyses the cycloaddition copolymerisation of diynes with elemental sulfur to afford poly(thiophene)s.

Recently we developed a transition metal-catalysed diyne cycloaddition copolymerisation as a new polymer synthesis and prepared various cycloaddition copolymers.[1] We thought that it would be interesting to exploit further this unique diyne cycloaddition copolymerisation. Here we report a new synthesis of poly(thiophene)[2] by the palladium-catalysed cycloaddition copolymerisation of a diyne with elemental sulfur S_8.

It is known that the cycloaddition of diphenylacetylene **1a** with S_8 occurs thermally at 200–210 °C in benzene to produce 2,3,4,5-tetraphenylthiophene **2a** [eqn. (1)].†,[3] We have now found that palladium acetate catalyses this cycloaddition (Table 1). The palladium-catalysed reaction at 160 and 140 °C afforded **2a** in good yield while the corresponding thermal reaction gave **2a** only in low yield. This result is noteworthy because, to the best of our knowledge, the reported thiophene formation by a transition metal (Co[4] and Rh[5])-catalysed alkyne–S_8 cycloaddition is limited to activated alkynes such as dimethyl acetylenedicarboxylate.

Based on these results, the $Pd(OAc)_2$-catalysed cycloaddition copolymerization of 1,4-bis(4′-hexylphenylethynyl)benzene **3b** with S_8 was carried out, eqn. (2). Two hexyl groups were introduced to 1,4-bis(phenylethynyl)benzene **3a** to improve the solubility of poly(thiophene).‡ The copolymerisation results are summarized in Table 2. Poly(thiophene) **4b** was isolated from the reaction mixture by evaporating under vacuum, adding THF (*ca.* 3 ml), cooling to −78 °C to precipitate most of the unreacted S_8, centrifuging, evaporating under vacuum, dissolving a copolymer in a small amount of CH_2Cl_2, adding diethyl ether (20 ml) to precipitate the copolymer, extracting contaminated S_8 with hot methanol,[6] and drying *in vacuo.* A large excess of S_8 to **3b** such as S : **3b** = 50 was necessary for effective copolymerisation. Compared to the thermal copolymerisation at 160 °C, where **4b** with a low molecular mass was produced only in 3% yield, catalysis by $Pd(OAc)_2$ was remarkable, affording **4b** with a molecular mass M_n (GPC) of 9800 in 32% yield. Prolonging the reaction time and decreasing the amount of solvent raised the copolymer yield and/or molecular mass. Compound **4b** was a dark brown powder and was soluble in $CHCl_3$, THF and toluene, but insoluble in methanol and diethyl ether.

Two control reactions confirmed **3b**–S_8 copolymerisation: (1) thermal and $Pd(OAc)_2$-catalysed homopolymerisations of **3b** without S_8 in toluene at 180 °C gave only the diyne oligomer **5**[1c] with a low molecular mass, which was isolated by preparative layer chromatography (PLC) [AcOEt–hexane = 1/100 (*v*/*v*)] and was soluble in diethyl ether and hexane, and (2) heating S_8 without **3b** in toluene at 180 °C in the presence and absence of $Pd(OAc)_2$ did not produce any polymeric material[7] detectable by GPC. For the formation of **4b**, other palladium complexes such as $Pd(OAc)_2(PPh_3)_3$ and $PdCl_2(MeCN)_2$ were



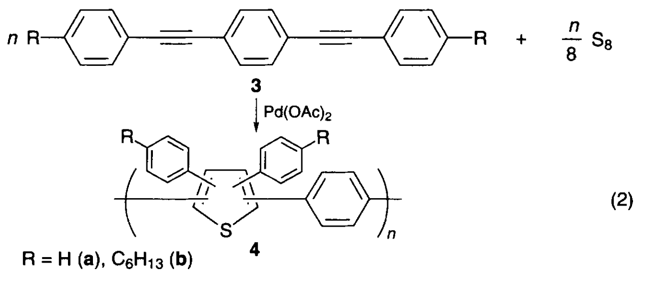


Table 1 Thermal and palladium-catalysed cycloaddition reactions of alkynes **1** with elemental sulfur S_8 to produce thiophenes **2** [eqn. (1)][a]

1	$Pd(OAc)_2$: **1**[b]	T/°C	Yield **2** (%)[c]	
a	0	180	**a**	89
	0.2	160		71
	0	160		14
	0.2	140		64
	0	140		3
b	0.2	180	**b**	63

[a] **1**, 0.5 mmol; S : **1** = 8; 2 ml toluene, 6 h. [b] A molar ratio. [c] Isolated yield by PLC based on the quantitative formation of **2**.

Table 2 Palladium-catalysed cycloaddition copolymerisation of diyne **3b** with elemental sulfur S_8 to produce poly(thiophene) **4b** [eqn. (2)][a]

				4b		
S:**3b**[b]	$Pd(OAc)_2$: **3b**[b]	T/°C	t/h	Yield (%)[c]	M_n[d]	M_w/M_n[d]
50	0.2	180	20	35	14000	1.8
50	0	180	20	25	12000	1.6
50	0.2	160	20	32	9800	1.5
50	0.2	160	20	43[e]	12300	1.5
50	0	160	20	3	2600	1.3
50	0.2	160	40	58	9400	1.7
50	0.2	140	20	11	3800	1.7
20	0.2	160	20	17	2700	1.3
8	0.2	180	20	28	9800	1.6
8	0.2	160	20	4	1900	1.3

[a] **3b**, 0.2 mmol; 4 ml toluene. [b] A molar ratio. [c] Based on the quantitative formation of **4b**. [d] Determined by GPC with polystyrene standards in $CHCl_3$. [e] 2 ml solvent.

also effective, but $Pd_2(dba)_3(CHCl_3)$ (dba = dibenzylideneacetone) was less effective.

The structure of **4b** was supported by IR, ^1H NMR and ^{13}C NMR spectroscopies. An IR absorption assignable to a thiophene ring appeared at 1488 cm^{-1}, which was not observed in the IR spectrum of the diyne oligomer **5**. The ^1H NMR spectrum of **4b** gave the most conclusive evidence of the poly(thiophene) structure: it showed five kinds of signals due to poly(thiophene) **4b** with reasonable peak areas.§ To confirm further the poly(thiophene) structure, model compound **2b** of a repeat unit of **4b** was prepared by the $Pd(OAc)_2$-catalysed reaction of (4-hexylphenyl)phenylacetylene **1b** and S_8 [eqn. (1), Table 1]. Partial agreement was observed between the ^{13}C NMR signals of **4b** and **2b**. Compound **2b** consisted of three regioisomers and had a complex C=C region in the ^{13}C NMR spectrum but the eight weak signals at δ 137.6–139.5 may be assigned to thiophene ring carbons. The corresponding signals of **4b** were observed at δ 137.0–140.5. Compound **4b** showed different ^{13}C NMR signals from those of **5** and did not exhibit the C≡C signals around δ 90. The ^{13}C NMR data are summarized in Fig. 1. Signals due to a hexyl group of **4b** agreed with those of **2b**. All these spectral findings support the poly(thiophene) structure of **4b**.

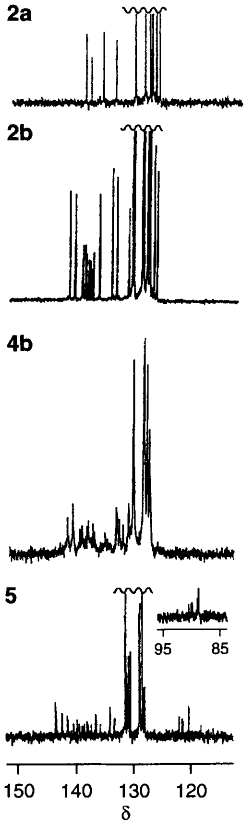


Fig. 1 ^{13}C NMR C=C and/or C≡C signals of 2,3,4,5-tetraphenylthiophene **2a**, 2,3,4,5-tetraarylthiophene **2b**, poly(thiophene) **4b** and diyne oligomer **5** ($CDCl_3$).

Footnotes

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† We examined the effect of solvent upon the thermal **1a**–S_8 cycloaddition, eqn.(1), (**1a**, 0.5 mmol; S : **1a** = 8; 2 ml solvent; 180 °C; 6 h). Yield (%) of **2a**: 68 (THF), 64 (benzene), 68 (toluene), 58 (MeCN) and 50 [1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone].

‡ A thermally-induced copolymerization of **3a** at 180 °C under the standard copolymerisation condition of Table 2 precipitated poly(thiophene) **4a** partly after the reaction was complete. Compound **4a** isolated [M_n (GPC) = 5700] was less soluble compared to **4b**.

§ *Spectroscopic data* for **4b**: IR ν(film)/cm^{-1} 3023, 1598, 1512, 1488, 1465, 1408, 1377, 1115, 1019, 907, 836 and 733; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87 (br m, 6 H), 1.27 (br m, 12 H), 1.55 (br m, 4 H), 2.54 (br m, 4 H) and 6.60–7.20 (m, 12 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.1, 22.6, 28.8, 28.95, 28.98, 29.1, 31.05, 31.14, 31.2, 31.3, 31.7, 35.6, 35.7, 127.6, 127.7, 127.8, 128.2, 128.8, 128.9, 130.6, 131.4, 133.1, 133.4, 133.6, 134.2–136.5 (m), 137.0–140.5 (m), 141.0 and 142.0.

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Received, 11th March 1996; Com. 6/01679K