Cobalt-catalysed cycloaddition terpolymerisation of carbon monoxide with diynes and norbornadiene to form poly(enone)s

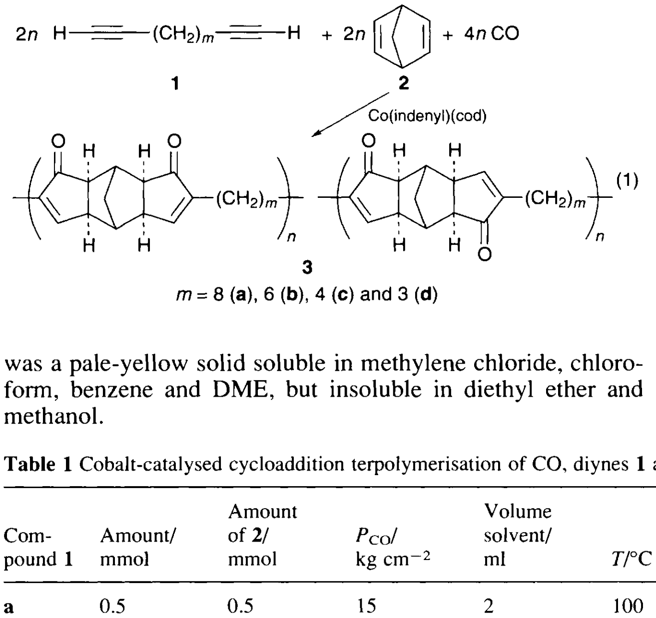
Tetsuo Tsuda*[a] and Fusahiro Tsugawa[b]

[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*

Co(indenyl)(cod)-catalysed cycloaddition terpolymerisation of CO with diynes $HC{\equiv}C(CH_2)_mC{\equiv}CH$ (m = 8, 6 and 4) and norbornadiene affords poly(enone)s.

Palladium-catalysed copolymerisation of CO with alkenes to produce poly(ketone)s by polyaddition reaction is well known.[1] Poly(amide) or poly(ester) synthesis from CO, dihalides and diamines or diols by palladium-catalysed polycondensation has also been reported.[2] Here we report a cobalt-catalysed cycloaddition terpolymerisation of CO, a diyne and a diene to afford a poly(enone), which is a new type of transition metal-catalysed CO incorporation into a polymer based on the Pauson–Khand reaction.[3,4]

Reactions were carried out in a 50 ml stainless steel autoclave under ntirogen. When an equimolar mixture of dodeca-1,11-diyne **1a** and norbornadiene **2** was treated with CO (15 kg cm^{-2}) in DME at 100 °C for 20 h in the presence of a Co(indenyl)(cod) catalyst[3] (5 mol%), poly(enone) **3a** with a GPC molecular mass M_n of 6700 (M_w/M_n = 2.9) was obtained in 54% yield by concentration of the reaction mixture under vacuum after filtration and by precipitation with methylene chloride–diethyl ether, eqn. (1). The poly(enone) **3a** obtained was a pale-yellow solid soluble in methylene chloride, chloroform, benzene and DME, but insoluble in diethyl ether and methanol.



Terpolymerisation results under various conditions are summarized in Table 1. Raising the reaction temperature, increasing the CO pressure and prolonging the reaction time did not improve the yield and molecular mass of **3a**. A **2** : **1a** molar feed ratio influenced the terpolymerisation although the present terpolymerisation based on the Pauson–Khand reaction[4] may proceed *via* a step growth polymerisation process: **3a** with a higher M_n of 9000 was obtained in the terpolymerisation with **2** : **1a** = 0.8. A similar reaction in benzene or THF produced an insoluble terpolymer while a terpolymerisation in a more diluted solution afforded soluble **3a**, Table 1.

The terpolymer structure was determined by IR, ^{1}H and ^{13}C NMR spectroscopy.† It is reasonable to assume that **3a** has two kinds of repeat units, eqn. (1). To confirm these terpolymer repeat units, two model compounds **A** and **B** were isolated by a Co(indenyl)(cod)-catalysed reaction of pentyne, **2** and CO, eqn. (2). Their regio- and stereo-chemistries were determined based on a ^{1}H NMR NOE measurement of **A**. **A** and **B** show ^{13}C NMR C=O peaks at δ 209.1 and 209.7 and C=C peaks at δ 149.8 and 157.4, and 149.9 and 157.5, respectively. Compound **3a** prepared from **2**/**1a** = 0.8 has ^{13}C NMR C=O peaks at 209.1 and 209.7 and C=C peaks at δ 150.0, 150.1, 157.2 and 157.4.† Thus excellent agreement between the ^{13}C NMR C=O and C=C peaks of poly(enone) **3a** and the two model compounds **A** and **B** was observed. This fact demonstrates that the cobalt-catalysed cycloaddition terpolymerisation of CO, **1a** and **2** occurred to afford poly(enone) **3a**.

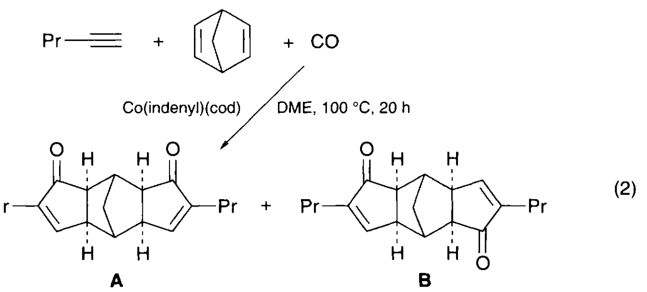


Table 1 Cobalt-catalysed cycloaddition terpolymerisation of CO, diynes **1** and norbornadiene **2** to produce poly(enone)s **3**, eqn. (1)[a]

Compound **1**	Amount/ mmol	Amount of **2**/ mmol	P_{CO}/ kg cm^{-2}	Volume solvent/ ml	T/°C	t/h	Product **3**	Yield (%)[b]	M_n[c]	M_w : M_n[c]
a	0.5	0.5	15	2	100	20	**a**	46	6100	1.6
a	0.5	0.5	15	2	100	40	**a**	48	5100	2.4
a	0.5	0.5	15	2	120	20	**a**	42	4200	2.0
a	0.5	0.5	50	2	100	20	**a**	32	5700	3.9
a	1	1	15	2	100	20	**a**	54	6700	2.9
a	1	0.8	15	2	100	20	**a**	43	9000	2.0
a	1	0.6	15	2	100	20	**a**	49	7300	1.2
a	1	0.8	15	6	100	20	**a**	76[d]	6100	2.5
b	1	0.8	15	2	100	20	**b**	30	5700	1.5
c	1	0.8	15	2	100	20	**c**	56	4900	2.9
d	2	1.6	15	2	100	20	**d**	31	1600	1.5

[a] Co(indenyl)(cod) : **1** = 0.05; DME. [b] Based on the quantitative formation of **3**. [c] Determined by GPC with polystyrene standards in $CHCl_3$. [d] Benzene.

The ^{1}H NMR spectrum of **A** showed a separate signal at δ 2.57 ascribable to a bridgehead proton near to a carbonyl group. The corresponding signal was clearly observed in the ^{1}H NMR spectrum of **3a**. The molar ratio of the two types of repeat units in **3a** was determined to be 1.0 using the signal peak area characteristic of the repeat unit related to **A**.

Other diynes $HC{\equiv}C(CH_2)_mC{\equiv}CH$ with different methylene chains **1b** (m = 6) and **1c** (m = 4) also underwent terpolymerization with CO and **2** to afford the corresponding poly(enone)s **3b** and **3c**, which were identified by IR, ^{1}H and ^{13}C NMR spectroscopy and are similar to **3a**. Hepta-1,6-diyne **1d** (m = 3) gave only a terpolymer with a low molecular mass, Table 1.

The thermal stability of **3a** was examined by thermogravimetric analysis (TGA) under air. The temperature causing a 10% weight loss, T_{10}, was 395 °C.

Footnote

† *Spectroscopic data* for **3a**: IR (film)/cm^{-1} 3035, 1698, 1626, 917 and 732; ^{1}H NMR (270 MHz, $CDCl_3$) 0.75 (br s, 4 H), 1.08–1.56 (m, 24 H), 1.98–2.20 (m, 9 H), 2.20–2.38 (m, 6 H), 2.57 (br s, 1 H), 2.63–2.80 (m, 4 H) and 7.09 (br s, 4 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) 24.1, 24.4, 24.7, 27.7, 29.1, 29.3, 40.2, 40.5, 47.4, 48.3, 52.7, 53.7, 150.0, 150.1, 157.2, 157.4, 209.1 and 209.7

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