Copolymers of vinyl epoxides with carbon monoxide†

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Highly functionalized alternating polyketones which possess epoxide groups in the side chains are synthesized by cationic palladium(II) complex catalyzed copolymerization of vinyl epoxides (non-conjugated diene monoepoxides) with carbon monoxide. Catalytic amounts of formic acid and 1,4-naphthoquinone promote the copolymerization significantly without effecting the epoxide group, with $[Pd(L)(MeCN)_2](BF_4)_2$ (L = (R,R)-Me-DUPHOS) as the catalyst.

Alternating aliphatic polyketones, a new class of engineering thermoplastics made from alk-1-enes and CO, have attracted great interest in polymer science in recent years.[1] The monomers are readily available in high purity and at a relatively low cost, and the polyketones have interesting and unique properties, and may replace conventional engineering thermoplastics in several areas of application (*e.g.* polyketone derived from ethylene and CO).[2]

Another important aspect of polyketones is the presence of carbonyl groups in the polymer backbone that makes them suitable for functional group modifications,[3] and hence polyketones which possess other functional groups in the side chains can serve as excellent starting materials or pre-polymers for other classes of valuable polymers. One of the major goals in this area is the synthesis of highly functionalized polyketones from functionalized alkenes and CO. There are very few examples of the copolymerization of functionalized alkenes with CO.[4–9]

A number of cationic palladium(II) complexes with weakly or non-coordinating counteranions, and phosphine or nitrogen ligands, have been used for the copolymerization of olefins with CO. In the case of higher α-olefins, using a chiral bidentate ligand can afford optically active copolymers with nearly complete head-to-tail regioselectivity and isotacticity, higher molecular weights and higher polymer yields compared to other achiral bidentate ligands.[5,7–9]

The epoxide group is one of the most versatile and important functional groups in organic synthesis. We now wish to report the synthesis of alternating highly functionalized polyketones, which possess epoxide groups in the side chains, *via* cationic palladium(II) catalyzed copolymerization of vinyl epoxides with CO. Given the facility with which epoxides undergo palladium catalyzed rearrangment[10] and other reactions of epoxides, the selectivity for the olefinic unit in the reactions described herein, is indeed impressive.

We first examined the copolymerization of 1,2-epoxyhex-5-ene with CO as a model reaction using, as catalyst, various kinds of cationic palladium(II) complexes with bidentate or monodentate chiral and achiral phosphine ligands [reaction (1)].
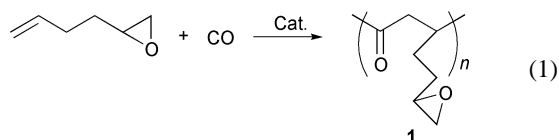
$$(1)$$

Among the reported catalyst systems, only $[Pd(L)(MeCN)_2](BF_4)_2$ (L = (R,R)-Me-DUPHOS, Me-DU-PHOS = 1,2-bis(2,5-dimethylphospholano)benzene) previously used for the copolymerization of functionalized ($-CO_2H$ or $-OH$) alkenes with CO by Sen and co-workers,[5] gave traces of co-oligomer when 1,2-epoxyhex-5-ene was reacted with CO (1000 psi) at 40 °C, in nitromethane and $CHCl_3$ (run 1, Table 1). Quinones are known to promote the copolymerization,[11] so we examined the effect of quinones as a promoter. 1,4-Naphthoquinone gave better results than other quinones such as 1,4-benzoquinone or 2-*tert*-butyl-1,4-benzoquinone. Repetition of the same reaction in the presence of a catalytic amount (3.1 mol%) of 1,4-naphthoquinone afforded the corresponding copolymer (**1**) in moderate molecular weight but in only 10% yield (run 2, Table 1). We then searched for another promoter or coinitiator which could enable this copolymerization to occur without effecting the epoxide group. It was found that a catalytic amount of HCO_2H can significantly improve the yield of the epoxypolyketone. When the copolymerization was performed in the presence of a catalytic amount of 1,4-naphthoquinone and HCO_2H as promoters, as well as the palladium complex, up to 63% yield of copolymer **1** was obtained in moderate molecular weight (run 4, Table 1). Even HCO_2H alone can be used as a promoter with copolymer **1** formed in 26% yield but the molecular weight was lower than using only 1,4-naphthoquinone (compare runs 2 and 7, Table 1). The exact role of HCO_2H is not clear but it can possibly generate palladium hydride, which is known as an active catalyst [reaction (2)].[1c,12] The effect of monomer concentration
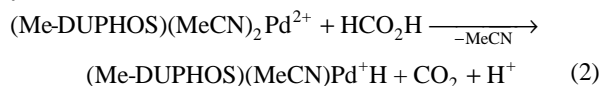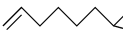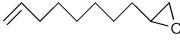
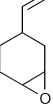$$(\text{Me-DUPHOS})(\text{MeCN})_2\,\text{Pd}^{2+} + \text{HCO}_2\text{H} \xrightarrow{-\text{MeCN}}$$

$$(\text{Me-DUPHOS})(\text{MeCN})\text{Pd}^+\text{H} + \text{CO}_2 + \text{H}^+ \quad (2)$$
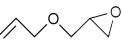
Table 1 Copolymerization of 1,2-epoxyhex-5-ene with CO[a]

		Promotor			Result	
Run	[Epoxide]/ M	1,4-NQ/ mmol	HCO_2H/ mmol	Time/ h	Yield (%)	M_w[b] M_w/M_n
1	2	—	—	24	trace	— 19 700
2	2	0.25	—	24	10	1.99 12 900
3	2	0.25	0.3	18	40	1.58 15 500
4	2	0.25	0.6	18	63	1.72 12 300
5	1.33	0.25	0.6	18	47	1.61 10 900
6	1.33	0.25	0.6	30	67	1.97 12 200
7	2	—	0.6	24	26	1.62 11 600
8[c]	2	0.25	0.6	24	46	2.03
9[d]	2	0.25	0.6	24	Trace	—

[a] Condition: 1,2-epoxyhex-5-ene 8 mmol, solvent; CH_3NO_2 + $CHCl_3$ (ratio 1:1) 4 ml ([Sub]/M = 2); [Pd(MeCN)$_4$](BF$_4$)$_2$, 0.02 mmol (0.25 mol%); (R,R)-Me-DUPHOS, 0.02 mmol (0.25 mol%), CO, 1000 psi, temp. 40 °C. [b] Molecular weights were measured by GPC relative to polystyrene standards. [c] CH_3NO_2 only as solvent. [d] $CHCl_3$ only as solvent.

Table 2 The copolymerization of vinyl epoxides with CO[a]

Run	Epoxide	Time/h	Copolymer, yield (%)	M_w (M_w/M_n)[b]
1		40	**3**, 58	30 500 (1.97)
2		40	**4**, 52	33 600 (1.41)
3		18	**5**, 41	28 500 (3.40)
4		48	**6**, 77	3 350 (1.28)
5		24	—	—

[a] Reaction conditions were the same as for run 4 in Table 1. [b] Molecular weights were measured by GPC relative to polystyrene standards.

was not critical but higher concentrations afforded higher molecular weights for the epoxypolyketones (run 4–6, Table 1). A 1 : 1 (v/v) mixture of nitromethane and CHCl₃ was the best solvent system. Use of only chloroform as the solvent gave trace amounts of copolymer **1** (run 9, Table 1) while use of only nitromethane gave lower yields than the mixed solvent system (run 8, Table 1).

The above results indicate that the optimum conditions for the copolymerization of 1,2-epoxyhex-5-ene with CO are 0.25 mol% of [Pd(MeCN)₄](BF₄)₂, 0.25 mol% of (R,R)-Me-DU-PHOS, 3.1 mol% of 1,4-naphthoquinone and 7.5 mol% of HCO₂H in nitromethane and solvent at 40 °C under 1000 psi of CO (run 4, Table 1).

Under the optimum reaction conditions, principally the poly(1,4-ketone) structure (**1**) of the corresponding copolymer was obtained and soluble in organic solvents like CH₂Cl₂, THF or DMSO. However if the copolymerization was performed for an extended reaction time (more than 24 h) or isolated as a pure solid, the structure of the copolymer was that of a poly-(spiroketal-1,4-ketone) which is insoluble in common organic solvents and even in fluorinated alcohols. The solid state ¹³C NMR spectrum of the poly(spiroketal-1,4-ketone) indicated a 1 : 1 ratio of the poly(1,4-ketone) and poly(spiroketal), with resonances of 1,4-keto groups and spiroketal groups appearing at 211.5 and 110.5 ppm respectively. The values of 1,4-keto and spiroketal groups of other polyketones (higher α-olefins or other functionalized alkenes and CO) occur at 211–214 and 112–114 ppm respectively.[5,8] The structure of the copolymer **1** (*i.e.* poly(1,4-ketone)) was determined by ¹³C NMR and IR, and was supported by elemental analysis.† The IR spectrum displays a carbonyl stretching band at 1706 cm⁻¹, and the epoxy group bands appeared at 1260, 914 and 835 cm⁻¹. The ¹³C NMR spectrum (DMSO-d₆) showed a resonance at 211.8 ppm due to the carbonyl group, and resonances at 44.5 and 43.5 ppm which are due to the CH₂CH units in the polymer backbone. Resonances at 51.5 and 46.5 ppm are due to the epoxide carbons in the side chains and the (CH₂)₂ units in the side chains appeared at 29.4 and 27.3 ppm. The chemical shift values for the carbonyl and main chain carbons of the ¹³C NMR spectrum, and the simplicity of the spectrum, support the copolymerization as a highly regio (head-to-tail) and diastereoselective (isotactic) process.[5,7,8]

Several other vinyl epoxides were copolymerized with CO under the optimum reaction conditions found for the copolymerization of CO and 1,2-epoxyhex-5-ene (run 4, Table 1), and the results are summarized in Table 2.†

In the case of 1,2-epoxyoct-7-ene, where the epoxy group is far from the olefinic unit compared with 1,2-epoxyhex-5-ene,

the copolymerization was slower but the molecular weight of the copolymer **3** was higher than that of **1** (run 1, Table 2). 1,2-Epoxydec-9-ene gave similar results to that of 1,2-epoxy-oct-7-ene, affording **4** but with narrower polydispersity when compared with 1,2-epoxyhex-5-ene and 1,2-epoxyoct-7-ene (compare run 6, Table 1, run 1 and 2, Table 2). The copolymerization of 4-vinyl-1,2-epoxycyclohexane (*cis* and *trans* mixture) with CO afforded the corresponding copolymer **5** in reasonable yield and molecular weight, but with broad polydispersity ($M_w/M_n = 3.40$, run 3, Table 2). Allyl glycidyl ether, which has not been successfully copolymerized with CO in the past,[4] can also undergo smooth copolymerization under the reaction conditions described above, affording the copolymer **6** in 77% yield. Interestingly, the molecular weight was very low ($M_w = 3350$, run 4, Table 2) compared to vinyl epoxides not having an ether group. The copolymer **6** was slightly soluble in DMSO, and the molar optical rotation was + 3.4° ($c = 6.1$ mg ml⁻¹, DMSO). Finally in the case of conjugated diene monoxide, 1,2-epoxybut-3-ene, the copolymerization with CO did not proceed under the usual conditions, and the starting epoxide was recovered unchanged (run 5, Table 2).

In conclusion, the copolymerization of vinyl epoxides and CO proceeds in good yields and moderate molecular weights, in the presence of [Pd((R,R)-Me-DUPHOS)(MeCN)₂](BF₄)₂ as the catalyst, with HCO₂H and 1,4-naphthoquinone as promoters. Complete chemoselectivity was observed, even in the presence of a reactive epoxide group. These polyketones, with epoxides in the pendant chain, will be of considerable value as precursors to novel polymeric materials by ring opening reactions of the epoxide groups.

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