

Palladium catalysed copolymerisation of ethene with alkylacrylates: polar comonomer *built into* the linear polymer chain†

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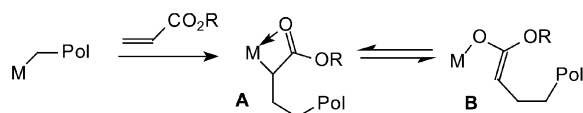
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Copolymerisation of ethene and alkylacrylates is catalysed by palladium modified with di(2-methoxyphenyl)phosphinobenzene-2-sulfonic acid (DOPPBS); a linear polymer is produced in which acrylate units are incorporated into the polyethylene backbone.

Early transition metal Ziegler–Natta type complexes are used extensively for the polymerization of ethene and propylene. In recent years, late transition metal catalysts have attracted attention not only for the polymerisation of these non-polar olefins, but more importantly for the copolymerisation of hydrocarbon monomers with readily available polar monomers such as acrylates and vinyl acetate.¹ Currently, commercial processes for the copolymerisation of these monomers require radical routes that often require high pressure, thus limiting the range of materials available. There is therefore a need for new molecular catalysts capable of copolymerising hydrocarbon and polar monomers under milder conditions in a more controlled fashion.

Some early transition metal catalysts have been shown to catalyse block copolymerisation of, for example ethene and acrylates,² however late transition metal catalysts have shown the most promise for polar comonomer incorporation, but in the majority of cases the polar functionality is remote from the vinyl group.³ This can be understood by considering the intermediate formed when, for example, an acrylate unit is inserted in a 2,1-fashion into a metal–carbon bond. The enolate **B** formed is inert to further olefin insertion.



† Electronic supplementary information (ESI) available: NMR data for entries 1, 9, 10, 12 and size exclusion chromatographic data for entries 1, 3, 8, 12. See <http://www.rsc.org/suppdata/cc/b1/b111252j/>

Brookhart *et al.* have subsequently shown that vinyl monomers can be copolymerised with ethene and propylene using cationic α -diimine palladium catalysts, yielding highly branched polymers.⁴ The branching reflects the catalyst ‘walking away’ from the acrylate unit, isolating it at the chain end. The random incorporation of polar comonomers into linear polyethylene by transition metal catalysed insertion polymerisation has yet to be demonstrated.⁵

The use of neutral oxygen-containing metal chelates as catalysts was developed many years ago by Keim for the Shell higher olefin process (SHOP)⁶ in which [P,O]Ni catalysed ethene oligomerisation shows high tolerance for functional groups.^{3a} Grubbs and coworkers recently developed a family of [N,O]Ni catalysts capable of copolymerising ethene and functionalised norbornenes,^{3c} and Gibson *et al.* employed [P,O]Ni catalysts to produce low molecular weight methylmethacrylate(MMA)-terminated polyethylene.⁷

Building on work carried out previously in these laboratories,^{3b,8} we report here a neutral Pd catalyst formed *in situ* by combination of Pd(OAc)₂ or Pd(dba)₂ (dba = dibenzylideneacetone) and [P,O] ligand **1**,⁹ capable of copolymerising ethene and acrylates. NMR analysis of the copolymer shows *ca.* 10% acrylate units *incorporated* into the linear polyethylene backbone, consistent with a mechanism that involves direct ethene insertion into the palladium chelate **A**. The results from the copolymerisation experiments (below) are shown in Table 1.

Catalyst activities are modest, reflecting the thermodynamic barrier in reacting chelate **A** with C₂H₄. The C₂H₄/methylacrylate (MA) copolymerisation was carried out in ethanol (entries

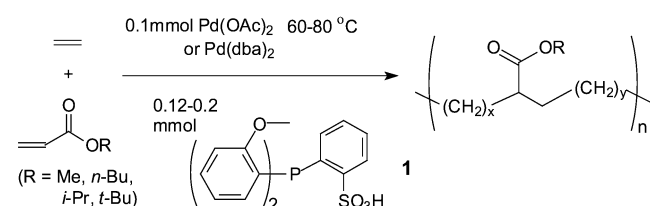


Table 1 Ethene (30 bar)-acrylate copolymerisation data‡

Entry	Pd/ mmol	[P-O]/ mmol	Solvent/ ml	Acrylate/ ml	Time/ h	T/ °C	Polymer yield/ g	Activity ^a / gmmol ⁻¹ h ⁻¹	Acrylate incorporation ^b / %	M _n ^c	M _w /M _n
1	Pd(dba) ₂ 0.1	0.12	ethanol 25	methyl acrylate 25	5	70	2.1	4	10	5 500	1.6
2	“	“	ethanol 10	methyl acrylate 40	10	80	9	9	17	6 400	1.8
3	“	“	toluene 25	methyl acrylate 25	15	80	8.5	6	13	12 800	1.6
4	Pd(OAc) ₂ 0.1	0.2	toluene 40	methyl acrylate 10	5	“	5.1	10	7	9 500	2.4
5	“	“	diglyme 40	methyl acrylate 10	10	“	18.4	18	9	7 600	2.4
6	Pd(OAc) ₂ 0.25	0.5 ^d	“	“	5	“	11.0	9	3	3 900	nd
7	Pd(OAc) ₂ 0.1	0.12	“	“	10	“	10.5	11	5	10 000	2.1
8	“	“	diglyme 25	methyl acrylate 25	10	“	7.5	8	10	11 800	1.6
9	Pd(dba) ₂ 0.1	0.12	toluene 25	<i>i</i> -propyl acrylate 25	10	70	16.8	17	7	9 500	2.0
10	“	“	“	<i>n</i> -butyl acrylate 25	10	60	9.9	10	9	14 000	2.0
11	“	“	toluene 20	<i>t</i> -butyl acrylate 30	10	60	16	16	2 ^e	21 100	2.9
12	“	“	—	<i>t</i> -butyl acrylate 40	15	70	19.5	13	10	15 000	1.7

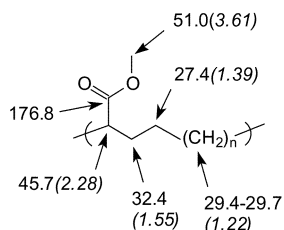
^a Based on Pd. ^b In mol %, based on ¹³C NMR data (measured in CDCl₃). ^c Determined by SEC vs polystyrene standards, uncorrected.

^d Diphenylbenzenesulfonic acid (DBPS). ^e Measured in 1,2,4-trichlorobenzene–C₂D₂Cl₄.

1,2), toluene (entries 3,4) and diglyme (entries 5–8); comparison of entry 7 with 8 demonstrates that unsurprisingly, higher acrylate concentration increases its incorporation at the expense of catalyst activity. Other alkylacrylates can also be copolymerised with ethene (entries 9–12); in the case of *tert*-butylacrylate, the comonomer had to be used as solvent to achieve significant incorporation. Entry 6 is included as a direct comparison with the DPBS system;⁷ the *o*-methoxy groups produce a more active catalyst which gives higher molecular weight polymer with more acrylate built in. The high amount of acrylate incorporation in these polymers is also manifested in their solubility in solvents such as chloroform and thf. The copolymer average molecular weights range from 5500–21000 (depending on solvent, alkylacrylate and their concentrations) with narrow molecular weight distributions.¹⁰

The mode of acrylate incorporation was unambiguously determined by a combination of ¹H, ¹H-COSY, ¹³C{¹H}, ¹³C DEPT and ¹H-¹³C correlation NMR spectroscopy (Fig. 1).¹⁰

Bulk polymer
¹³C NMR chemical shifts (δ),
¹H NMR shifts in parentheses

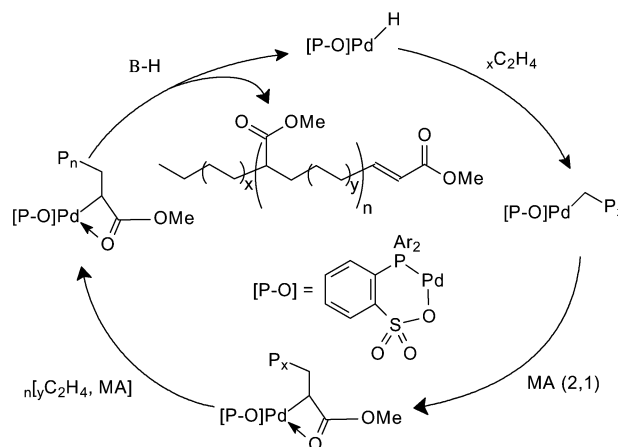


End groups	¹ H	¹³ C		¹ H	¹³ C
w	a 4.91	114.0	y	a 0.84	14.0
	b 5.77	139.1		b 1.26	22.9
	c 1.99	33.9		c nd	32.0
	d 1.32	nd			
x	a 1.09	17.0	z	a 3.67	51.0
	b 2.38	39.4		b -	167.0
	c -	176.8		c 5.77	120.9
	d 3.6	51.0		d 6.9	149.5
	e nd	33.7		e 2.14	32.1
	f nd	29.5		f 1.41	nd

Fig. 1 ¹H and ¹³C{¹H} data for copolymer (entry 1); nd = not determined due to overlapping resonances; w:x:y:z ≈ 3:1:3:1.

The simplicity of the ¹³C{¹H} NMR spectrum reflects the copolymer linearity, in contrast to the highly branched copolymer reported by Brookhart and coworkers.^{4a} The ¹³C{¹H} NMR spectrum of polymethylacrylate extracted by acetone during the work-up was also measured ([CH(CO₂CH₃)CH₂]_n, δ (¹³C) in CDCl₃: 51.5 (–OCH₃), 174.9 (–C(O)O), 41.0 (–CH–) and 34.7 (–CH₂–) ppm). No double acrylate insertions are detected by NMR in the copolymer on the basis of this and other⁵ data, and we propose a statistical distribution of ethene between acrylate units depending on the overall amount of incorporated polar comonomer.¹¹ End group determination was possible for this lower *M_w* copolymer, showing a predominance of ethene-initiated/acrylate-terminated polymer. This is also evident from the size exclusion chromatography (SEC) results for all the polymers; lower molecular weight copolymer contains slightly more acrylate comonomer,¹⁰ consistent with a reduced probability of propagation *vs.* termination after acrylate insertion compared to ethene insertion.

The proposed mechanism for the dominant ethene-initiated/acrylate-terminated copolymer is shown in Scheme 1. We assume a [P–O] chelate Pd hydride active catalyst species, based on the observed copolymer end groups, and the thoroughly studied analogous neutral [P–O]Ni chelates;^{2,3a,c,6,7} our same system with Ni(COD)₂ forms an active catalyst for polyethylene formation, but also^{3a} becomes poisoned by the presence of alkylacrylates. Using two equivalents of ligand per Pd does not appear to affect catalytic performance, indicating that inactive bis-chelates are not formed. Inspection of end groups **x** and **z** shows that acrylate clearly inserts in a 2,1-mode



Scheme 1 Proposed mechanism for formation of C₂H₄-initiated/MA-terminated copolymer.

for initiation and termination; it is therefore reasonable to assume that 2,1-insertion will also prevail in the chain. Further ethene insertion into the Pd-alkyl is presumably facilitated by destabilisation of the oxo-chelate; a combination of O-donation from the sulfonate group and the two *o*-methoxy groups apparently modify the palladium centre to an extent that enolate formation is suppressed relative to insertion of C₂H₄ into the neutral species **A**.

In summary, the results presented here constitute the first example of true transition metal catalysed ethene–alkylacrylate copolymerisation, generating copolymers with acrylate units built into the linear polyethylene backbone.

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Notes and references

‡ Typical reaction conditions: 0.1 mmol (57 mg) Pd(dba)₂ and 0.12 mmol (46 mg) BDOPPBS were mixed in 25 ml toluene in the dry box prior to transferring to a 250 ml Hastelloy C autoclave with 25 ml methylacrylate (MA). The autoclave was closed, flushed 3 times with 40 bar N₂ and charged with 30 bar C₂H₄. After *ca.* 15 min the autoclave was heated to, and maintained at 80 °C for 15 hours by a Thermo-Electric temperature control unit. After this time, the cooled contents of the autoclave were poured onto 300 ml acetone, the polymer filtered, washed with 100 ml methanol and 2 × 50 ml acetone and dried *in vacuo*.

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- The free ligand is a zwitterion; for synthesis, see reference 3b.
- For NMR and SEC data, see electronic supplementary information†.
- As expected, increasing acrylate concentration leads to more polyacrylate formation, but no double acrylate insertions are observed in the copolymer. We conclude therefore that the polyacrylate formation is catalysed by a different species (*e.g.* radical).