Polycarboxylic Acids *via* Catalytic Hydrocarboxylation of Polybutadienes

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Polycarboxylic acids with a variety of different micro-structures have been prepared by homogeneous catalytic hydrocarboxylation of polybutadienes using palladium based catalysts; the microstructure of the product polymers depends upon that of the starting material as well as on the nature of the catalyst system, since selectivity between functionalisation at the backbone double bonds or at the terminal or internal carbon atom of the pendant double bonds can to some extent be engineered.

Polycarboxylic acids find a range of uses in *e.g.* surface coatings.[1] In general, polycarboxylic acids have been prepared by polymerization of *e.g.* acrylic acid or maleic anhydride either alone or as copolymers with other unsaturated feedstocks.[1] These polymers all have the carboxy function directly attached to the main chain of the polymer. We are interested in the properties of polymers in which carboxylic acid groups can be separated from the main chain by a flexible spacer group, so have extended studies we have already made on the introduction of functional groups into unsaturated polymers[2–4] to include hydrocarboxylation reactions. Polybutadienes are of special interest in this context, since they are available with a variety of different molecular weight ranges and with double bonds in the backbone of the polymer or pendant from the main chain. The relative ratios of the three types of double bond (*cis* or *trans* in the backbone or pendant) can be controlled during the polymerization process. A very brief report on the hydrocarboxylation of a polybutadiene containing 60% double bonds using $[PdCl_2(PPh_3)_2]$ in the presence of excess PPh_3 has appeared and indicates that, although some selectivity to functionalisation of the terminal carbon atom of the pendant double bonds is observed, high selectivity is not obtained.[5]

We have studied the hydrocarboxylation of a wide variety of different starting polybutadienes (see Tables 1 and 2) and find that different catalyst systems can lead to different selectivities. Using $[PdCl_2(PPh_3)_2]$–PPh_3, resonances are observed from three different types of carboxylic carbon atoms in the ^{13}C NMR spectrum. These arise from the carboxylic acid group directly attached to the backbone (δ 177) or to the terminal (δ 175) or internal (δ 173) carbon atom of the pendant double bonds.† Analysis of the relative amounts of

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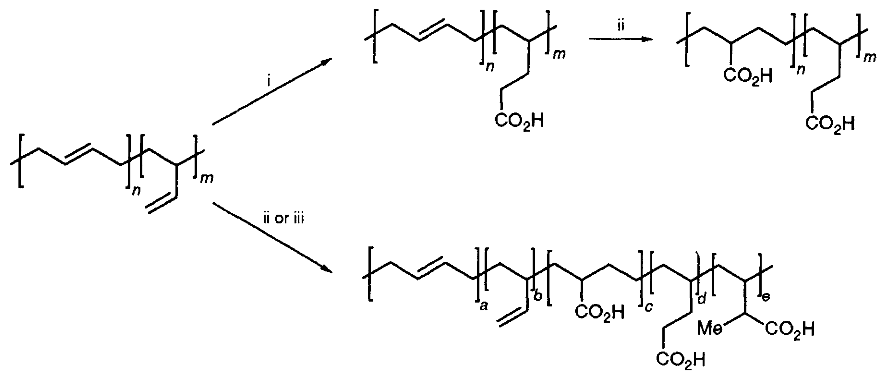
† These assignments arise because using the method described by Alper for hydrocarboxylation of all *cis*-polybutadiene only one resonance is observed, at δ 177, whilst using $PtCl_2(PPh_3)_2$–$SnCl_2$ for hydrocarboxylation of polymers containing pendant double bonds again gives only one resonance, at δ 175. ^1H NMR studies in this case show that only the pendant double bonds have been hydrocarboxylated.



Scheme 1 Synthesis of polycarboxylic acids *via* hydrocarboxylation of polybutadienes. Backbone double bonds can be *cis* or *trans*; only *trans* double bonds are shown. i, $[PdCl_2(PPh_3)_2]$–$SnCl_2$, methyl isobutyl ketone, 80 °C, 80 atm CO, 4 h; ii, $[PdCl_2(PPh_3)_2]$–PPh_3, benzene, 170 °C, 80 atm CO, 4 h, or iii, $PdCl_2$–$CuCl_2$–O_2 (0.5 atm), tetrahydrofuran, 25 °C, 0.5 atm CO, 24 h.

Table 1 Composition of starting and product polymers for hydrocarboxylation

		Double Bonds (%)[a]				Carboxylic acid (%)[b,c]			Carboxylic acid (%)[b,d]
Polymer	M_n	*cis*	*trans*	pendant	End group	backbone	terminal	branched	terminal
1	250 000 (M.W.)	100	0	0	H	82			0
2		20	60	20	OH				40
3	1500	30	42	27	Ph	54	78[e]		100
4	3400	22	50	26	Ph	81	81[e]		73
5	4500	23	37	40	H	83	58	15	100
6	1300	22	32	43	Ph		44	14	77
7	1000	12	19	53	Ph	81	81	9	100
8	1800	12	19	61	Ph				100
9	1480	0	16	81	CO_2H	75	32	10	83
10	3000	0	14	84	H				100
11	3000[f]	0	9	88	H				89

[a] % of different kinds of double bonds in starting polymer determined by ^1H and ^{13}C NMR. Where these do not sum to 100%, some butadiene units have been hydrogenated during the polymerisation process. [b] % conversion of different types of double bond to carboxylic acids; terminal is functionalisation at terminal C of pendant double bonds, branched is at internal C atom of pendant double bonds, backbone is at backbone double bonds. [c] $PdCl_2$–$CuCl_2$–O_2. [d] $[PdCl_2(PPh_3)_2]$–$SnCl_2$, backbone double bonds are unreactive. [e] Combined terminal and branched carboxylic acid yield. The signal intensity from branched carboxylic acid is too small to measure. [f] Narrow molecular weight distribution.

Table 2 Composition of polycarboxylic acid obtained from polymer **7** with different catalyst systems[a]

		Double bonds (%)			Carboxylic acid (%)		
Catalyst system		*cis*	*trans*	pendant	backbone	terminal	internal
i	$[PdCl_2(PPh_3)_2]$–$SnCl_2$	12	19	0	0	53	0
ii	$[PdCl_2(PPh_3)_2]$–PPh_3	4[b]		2	27	40	11
iii	$PdCl_2$–$CuCl_2$–O_2	6[b]		5	25	43	5
iv(a)	$[PdCl_2(PPh_3)_2]$–$SnCl_2$		0				
(b)	$[PdCl_2(PPh_3)_2]$–PPh_3						

[a] Each type of unit is expressed as a percentage of the original butadiene units in the starting polymer. [b] Combined yield of *cis* and *trans*.

the three types of carboxylic acid group formed indicates that, although the selectivity is low, there is a slight preference for carboxylation of the pendant double bonds over the backbone ones. The overall conversion of double bonds in this case is ~90%.

Similar results are observed using the elegant carboxylation system described by Alper[6] for simple carboxylic acids, $PdCl_2$–$CuCl_2$–O_2, which operates at ambient temperature and pressure, although this system is slightly less reactive. In Alper's work on simple alkenes, terminal alkenes have been shown to produce predominantly branched carboxylic acid. For polybutadienes, this is not the case and the reaction of the pendant double bonds shows substantial, although not total, selectivity towards terminal carboxylic acid formation. This difference in selectivity presumably arises from steric problems associated with the presence of the main chain on the carbon atom α to the internal carbon atoms of the pendant double bonds. A related effect can be noted[6] in the exclusive formation of 2,4-dimethylpentanoic acid on hydrocarboxylation of 4-methylpent-2-ene using the same system. Here, branching of the chain at the carbon α to the double bond apparently directs the incoming carboxylate group to the end of the double bond remote from the branching point. Maximum yields from this system for polymer carboxylation are *ca.* 80%, and there appears to be no particular correlation with the microstructure nor the average molecular weight (Table 3) of the polymer.

Using $[PdCl_2(PPh_3)_2]$–$SnCl_2$, which has been shown for

Table 3 Dependence of total conversion of unsaturated units to carboxylic acid upon number average molecular weight (M_n) of the polymer using the system $PdCl_2$–$CuCl_2$–O_2

Polymer	M_n	Overall conversion (%)
7	1000	87
6	1300	63
9	1480	47
3	1500	61
4	3400	82
5	4500	79
1	250000 (M.W.)	82

simple alkenes to give high selectivity to terminal carboxylic acids,[7] ^{13}C and ^{1}H NMR studies show that only one type of carboxylic acid is formed from all polybutadienes, with the functionalisation occurring on the terminal C atom of the pendant double bonds. Essentially complete hydrocarboxylation of the pendant double bonds occurs in many cases. It is possible to obtain a third type of polymer by sequentially applying $[PdCl_2(PPh_3)_2]$–$SnCl_2$ followed by $[PdCl_2(PPh_3)_2]$–PPh_3. In this case, complete hydrocarboxylation of all of the double bonds is observed and the pendant double bonds are selectively functionalized at the terminal C atom (Table 2). These reactions are outlined in Scheme 1.

In principle, the selectively functionalised polymers could be prepared by copolymerization of butadiene with pent-4-enoic acid but this does not appear to have been attempted. The relative scarcity of pent-4-enoic acid does not make this copolymerization reaction attractive. It is difficult to see that the other polymers could be readily prepared by routes other than those reported here so hydrocarboxylation is an attractive and simple route to a wide range of new polycarboxylic acids.

Unlike the starting polymers, which are generally syrupy liquids with glass transition temperatures (T_g) well below room temperature, the hydrocarboxylated polymers are solids which can be cast as films from solution, but which have T_g above room temperature, typically *ca.* 60 °C. They are soluble in polar organic solvents, *e.g.* acetone or methanol as well as in dilute NaOH, provided that the pH is kept $\geqslant 7$.

Preliminary studies suggest that they may have interesting properties in a range of different applications. For example, a product derived from polymer **7** with 35.5% hydrocarboxylation selectively on the terminal carbon atoms of the pendant double bonds, completely halted the uptake of water by partially wet balsa wood. Dry balsa wood (50 × 3 × 3 mm) was soaked in pure water for 52 h, during which time water had penetrated *ca.* 0.3 mm into the wood. The wood was then transferred into a solution containing 10% of the polymer and NaOH (pH 7). Further ingress of water has been prevented for 18 months as indicated by NMR imaging[8] and the observation that the wood still floats. In the absence of polymer, the wood becomes saturated and sinks within 16 days.

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