Synthesis of new functionalized polyenes by cooligomerization of butadiene with methyl acrylate on nickel catalysts

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Abstract

New polyenes are formed in protic media via nickel catalyzed cooligomerization of butadiene with methyl acrylate. High activities are achieved with amino-phosphinite ligands in aprotic solvent. Using a deuterium labeled ligand, the presence of the NH group of the ligand is shown to be the key point for the proton transfer involved in the mechanism.

1. Introduction

Homogeneous catalyzed linear cooligomerization of butadiene with methyl acrylate has already shown to produce two types of reaction according to the number of inserted butadiene units. Compounds with only one butadiene are mostly formed on cobalt [1] or palladium [2] catalysts, whereas compounds where two butadiene units are incorporated are preferentially formed on nickel based catalysts [3–6] (Scheme 1).

We have already reported that the use of nickel catalysts modified with amino-phosphinite (AMP) ligands is very efficient for linear dimerization of butadiene and its derivatives [7,8] as well as during butadiene functionalized dienes codimerization [9].

In this paper, we report the use of these ligands as modifier for nickel catalyzed methyl acrylate–

Scheme 1.
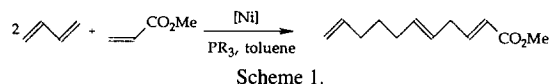
butadiene oligomerization, which will be shown to produce new functionalized polyenes.

2. Experimental

All experiments were carried out under nitrogen atmosphere using standard inert-atmosphere techniques.

The AMP ligands were synthesized by mono-phosphinylation of (1S,2R)-(+)-ephedrine (1 equiv.) with PPh_2NMe_2 or PCp_2Cl (1 equiv.) to lead to Ph–Ephos–NH or Cp–Ephos–NH (Scheme 2), respectively. The synthesis of the aryl ligand has already been described in the literature [10]. Cp–Ephos–NH was synthesized in the presence of an excess of triethylamine accord-

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D-(1S,2R)-Ephos-NH
δ(P-O) = 113.5 ppm

D-(1S,2R)-CpEphos-NH
δ(P-O) = 143.2 ppm

Cp = cyclopentyle

Scheme 2.
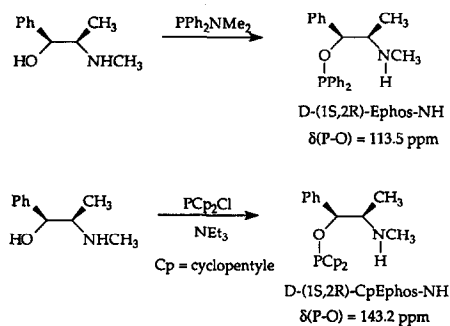
ing to a similar procedure and characterized by ^{31}P NMR (toluene-d_8 as solvent). The labeled (1S,2R)-Ephos–ND ligand was obtained by deuteration of the ephedrine precursor in presence of D_2O using a toluene reflux, followed by phosphinylation.

In a typical experiment, 0.0825 g (0.3 mmol) of bis(cycloocta-1,5-diene)nickel(0) (Ni(COD)$_2$) were weighed in a Schlenk tube. Then added successively were: the ligand (0.3 mmol) in toluene (8 ml) and methyl acrylate (1 g, 12 mmol) in heptane (2 g) used as internal standard. The red solution was frozen to −20°C. Liquid butadiene (1.3 g, 24 mmol) was then added. The mixture was heated to the desired temperature. Cooligomers 1 and 2 were separated by distillation followed by gas preparative chromatography on a DEGS column (4% chrom. WNAM 80–100 mesh, 4 m×¼ in.) (T = 195°C, $P(H_2) = 0.8$ bar).

These isomers were also separated by reaction with maleic anhydride. Only the oligomer 1 gives a Diels–Alder reaction to lead to an adduct 4 characterized by ^1H and ^{13}C NMR. This reaction was conducted on the mixture of cooligomers 1 and 2 by addition of maleic anhydride (1.1 equiv.) in toluene. The solution was refluxed during 2 h. After cooling, the solvent was evaporated and the Diels–Alder adduct 4 was separated from the cooligomer 2 by extraction with pentane.

^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 spectrometer. IR spectra were measured on a Perkin Elmer 683-PE 3500 data station. Mass spectra were recorded on a Nermag R1010B spectrometer.

3. Results and discussion

Upon using these AMP ligands as modifier during methylbutadiene acrylate dimerization, two new linear esters with a trienyl chain, methyl undeca-5E,8E,10-trienoate 1 and methyl undeca-5E,8Z,10-trienoate 2 are formed (Scheme 3).

Table 1 reports the results obtained with different Ni(COD)$_2$/AMP systems.

Without catalyst, only cyclohex-3-ene methylcarboxylate 3 is obtained, from the Diels–Alder reaction between butadiene and methyl acrylate. In the presence of zerovalent nickel, 1,5,9-CDT is formed in addition with 3. This product is formed from the coupling reaction between three butadiene units [11].

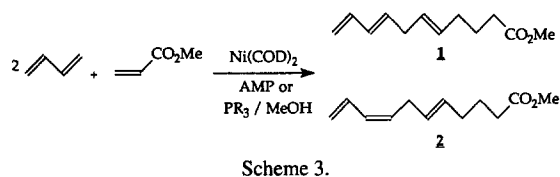The cooligomers 1 and 2 are major products on Ni(COD)$_2$/AMP catalysts. Octa-1,3,6-triene lin-

Scheme 3.

Table 1
'Methylbutadiene acrylate' cooligomerization on Ni(COD)$_2$/AMP catalysts

Entry	Ligand	Catalyst	t (h)	Conv. (%) [a]	Selectivity (%)
1	–	–	5	60	3 [d]: 100
2	–	Ni(COD)$_2$	4	70	3: 70 1,5,9-CDT [b]: 30
3	(+)-Ephos–NH	Ni(COD)$_2$	9	81	1: 43; 2: 15 1,3,6-OT [c]: 29 others: 13
4	(+)-CpEphos–NH	Ni(COD)$_2$	6	80	1: 50; 2: 28 1,3,6-OT: 13 others: 9

[a] Methyl acrylate (MA) conversion.
[b] CDT = cyclododeca-1,5,9-triene.
[c] 1,3,6-OT = octa-1,3,6-triene.
[d] 3 = cyclohex-3-ene methylcarboxylate.
Experimental conditions: Ni(COD)$_2$ = AMP = 0.3 mmol; solvent = toluene (8 ml); T = 80°C; internal standard = heptane (2 g); MA/Ni = 40; butadiene/Ni = 80.

Table 2
'Methylbutadiene acrylate' cooligomerization on $Ni(COD)_2/PR_3/$
CH_3OH catalysts

Entry	Ligand	t (h)	Conv. (%) [a]	Selectivity (%)
1	PPh_3	13	75	**1**: 43; **2**: 24 1,3,6-OT: 23; others: 10
2	$P(OPh)_3$	28	29	**1**: 10; **2**: 8; **3**: 37 1,5-COD: 25; others: 20

[a] Methyl acrylate (MA) conversion.
Experimental conditions: $Ni(COD)_2 = AMP = 0.3$ mmol; $CH_3OH = 30$ mmol; butadiene/Ni = 80; MA/Ni = 40; solvent = toluene (8 ml); $T = 80°C$; internal standard = heptane (2 g).

ear dimers cannot be avoided due to the high activity of this system on linear butadiene dimerization.

It is worth mentioning here that the cooligomers **1** and **2** have structures different from those reported in the literature for the same reaction conducted with $Ni(0)/PR_3$. Indeed, using $Ni(0)$ species with phosphines in toluene, methyl undeca-$2E,5E,9E$-trienoate isomer was obtained (Scheme SCHEME) [6].

Similar selectivities in **1** and **2** are obtained on $Ni(COD)_2/PR_3/CH_3OH$ systems (Table 2), although with a lower reaction rate as compared with the $Ni(0)/AMP$ catalysts.

One can suggest that the NH moiety in the AMP ligand is responsible for the oligomers **1** and **2** formation, via a mechanism similar to that demonstrated for the selective production of octa-1,3,6-trienes from butadiene [7]. In order to prove this mechanism, we have used the deuterated ligand $PPh_2OCH(Ph)CH(Me)NDMe$ (($1S,2R$)-Ephos–ND), in which the hydrogen of the NH is replaced by a deuterium. In this labeled experiment, a butadiene/nickel ratio of 5 and pentane as solvent were used, the reaction being stopped rapidly in order to avoid further production of unlabeled trienes. The oligomers **1** and **2** obtained by this reaction were separated and characterized by mass spectrometry. Fig. 1 and Fig. 2 compare the mass spectra of **1** from a labeled experiment and an unlabeled one.

The presence of a deuterium on **1** appears clearly because of the more important relative

abundance of m/e 195 in Fig. 1 compared to Fig. 2. In order to determine the position of the deuterium on the triene, we have compared all the fragments. The major peak at m/e 79 corresponds to the $C_6H_7^+$ fragment, stabilized by resonance. It is noteworthy that the relative abundances of the 79 and 80 ions are similar in the two cases, which indicates that no deuterium is incorporated in this fragment. On the other hand, we observe an increase of the relative abundance of the m/e 75 fragment as compared with 74 in the labeled olig-
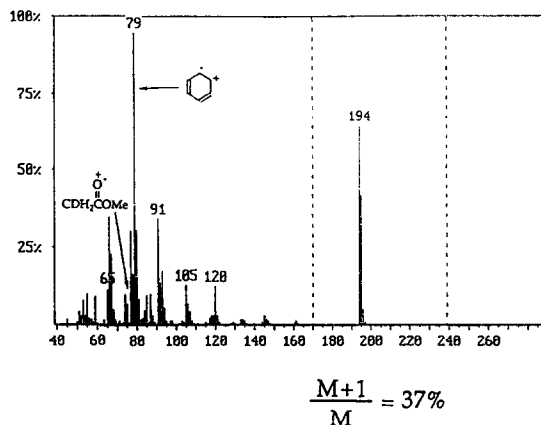

$$\frac{M+1}{M} = 37\%$$

Fig. 1. Mass spectrum of the labeled cooligomer.

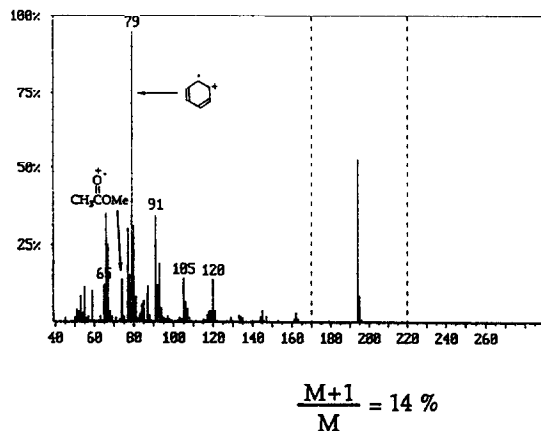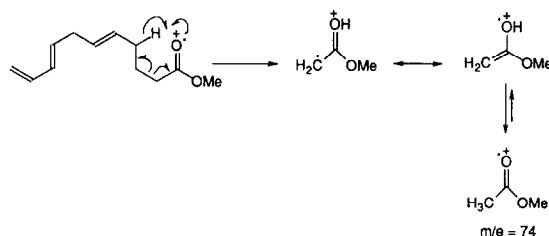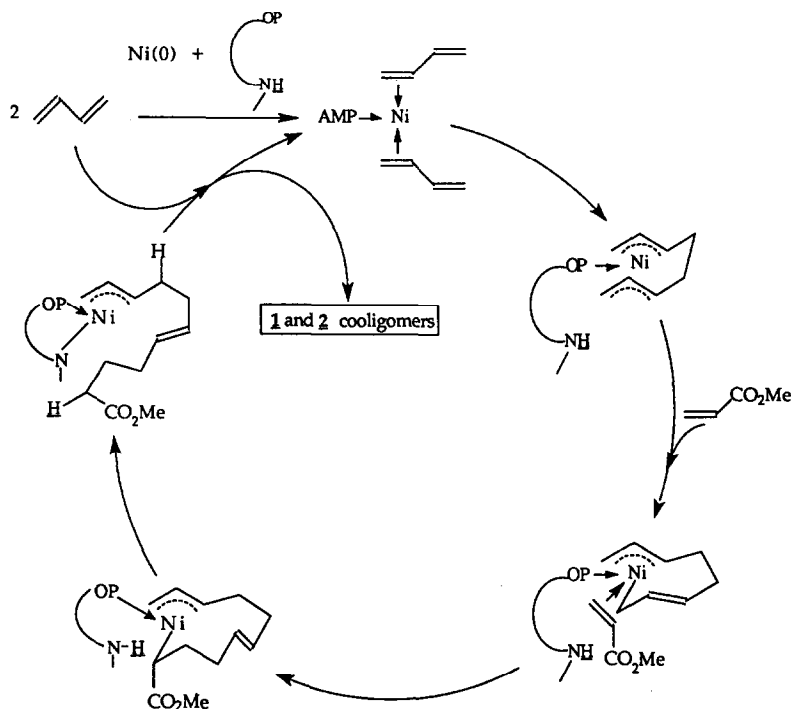

$$\frac{M+1}{M} = 14\%$$

Fig. 2. Mass spectrum of the unlabeled cooligomer.

$m/e = 74$

Scheme 4. Mc Lafferty rearrangement of **1**.

Scheme 5. Mechanism for linear 'methylbutadiene acrylate' cooligomerization.

omer. The m/e 74 fragment corresponds to $CH_2=C(O^+ \cdot H)OMe$ ion obtained by Mc-Lafferty rearrangement as shown in Scheme 4. Therefore, we can assume that the deuterium is transferred on this fragment $(CDH=C(O^+ \cdot H)OMe, m/e$ 75). We assign the presence of the deuterium at the C_2 atom carbon of the triene.

The presence of the deuterium exclusively at this position was confirmed by ^{13}C NMR and IR analyses on the labeled oligomer. By NMR, the emergence of a triplet at 33 ppm ($J_{C-D} = 20$ Hz) confirms the position of the deuterium at the C_2 carbon atom. As expected, an absorption band at 2170 cm^{-1} was observed by IR, which corresponds to the C–D bonding vibration frequency of a methylene group.

These studies confirm a mechanism of a proton transfer from the ligand–NH to the oligomer. This is in total agreement with the previous mechanism described for the butadiene dimerization [7]. We therefore propose the mechanism depicted in Scheme 5. The high activity with AMP ligands might be due to their specific structure. Indeed,

due to the fact that the phosphinite moiety coordinates the metal, the NH moiety is in close proximity to the nickel, which promotes the proton transfer reaction

Ni(0)/ligand/proton donor systems are therefore good catalysts for the cooligomerization of butadiene with methyl acrylate to produce new functionalized polyenes. Moreover, bifunctional AMP ligands are shown to be more efficient, as the process only uses 1 equiv. of phosphorus modifier without any other proton source, which could be useful in non protic solvents.

3.1. Spectroscopic characterization of the 1 and 2 cooligomers and the adduct 4

1 and 2 present two Z/E isomers in position 8–9. ^{13}C NMR allows us to know the stereochemistry of two double bonds separated by a sp^3 carbon [12]. Indeed, it has been shown that methylene ^{13}C chemical shifts surrounded by two double bonds depend on the stereochemistry of the double bonds, namely ca. 35, 30 and 25 ppm for *trans–trans*, and *trans–cis* and *cis–cis* [12].

That way, (E,Z) and (E,E) isomers have been characterized from ^{13}C NMR chemical shift of the carbon 7.

1
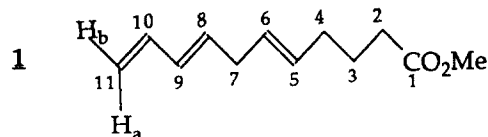
IR (cm^{-1}): 3087, 2997, 1733, 1651, 1173, 1007, 971, 911.

^{1}H NMR (CDCl$_3$): H$_3$: 1.7 (m; $^3J_{2-3} = 7.4$; 2H); H$_4$: 2.05 (m; $^3J_{4-3} = 8.4$; 2H); H$_2$: 2.3 (t; $^3J_{2-3}$; 7.4; 2H); H$_7$: 2.75 (dd ; 2H); OCH$_3$: 3.65 (s; 3H); H$_{11b}$: 4.95 (d; $^3J_{10-11b} = 12$; 1H); H$_{11a}$: 5.09 (d; $^3J_{10-11a} = 17$; 1H); H$_5$ and H$_6$: 5.42 (m; $J_{trans} = 11$; 2H); H$_8$: 5.67 (m; $^3J_{7-8} = 7$; 1H); H$_9$: 6.04 (m; 1H); H$_{10}$: 6.3 (m; $^3J_{9-10} = 17$; 1H).

^{13}C NMR (CDCl$_3$): C sp^2: 174 (CO); 115; 117.5; 127.3; 130.8; 132.2; 137. C sp^3: 24.4 (C$_3$); 31.7 (C$_4$); 33.1 (C$_2$); 34.8 (C$_7$); 51 (O–CH$_3$).

2
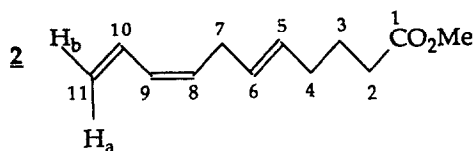
^{1}H NMR (CDCl$_3$): H$_3$: 1.65 (m; $^3J_{2-3} = 7.4$; 2H); H$_4$: 1.95 (m; $^3J_{4-3} = 8.4$; 2H); H$_2$: 2.15 (t; $^3J_{2-3} = 7.4$; 2H); H$_7$: 2.3 (dd ; 2H); OCH$_3$: 3.65 (s; 3H); H$_{11b}$: 5 (m; 1H); H$_{11a}$: 5.15 (m; 1H); H$_5$ and H$_6$: 5.4 (m; $J_{trans} = 11.3$; 2H); H$_8$ and H$_9$: 6.1 (m; $J_{cis} = 7$; 2H); H$_{10}$: 6.35 (m; 1H).

^{13}C NMR (CDCl$_3$): C sp^2: 174 (CO); 115; 118.2; 126.9; 131; 133; 135.2. C sp^3: 24.1 (C$_3$); 31.6 (C$_4$); 33 (C$_2$); 30.2 (C$_7$); 51.2 (O–CH$_3$).

4
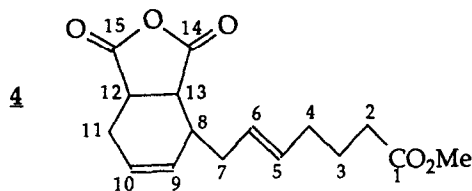
^{1}H NMR (CDCl$_3$): H$_3$: 1.7 (m; $^3J_{2-3} = 7.4$; 2H); H$_4$: 2 (m; $^3J_{4-3} = 8.4$; 2H); H$_2$, H$_7$ and H$_{11}$: 2.4 (m. 6H); H$_8$: 2.6 (m ; 1H); H$_{12}$ and H$_{13}$: 3.4 (m; $J_{13-8} = 6.7$; 2H)–OCH$_3$: 3.7 (s; 3H); H$_5$ and H$_6$: 5.5 (m. 2H); H$_9$ and H$_{10}$: 5.9 (m; 2H).

^{13}C NMR (CDCl$_3$): C sp^2: 174.1; 174.3; 174.5 (3 CO); 125.2 (C$_6$); 127.8 (C$_5$); 132.5 (C$_9$); 133.2 (C$_{10}$). C sp^3: 24.4 (C$_3$); 29.7 (C$_4$); 31.8 (C$_{11}$); 33.3 (C$_7$); 35.7 (C$_2$); 40.9 (C$_8$); 43.3 (C$_{13}$); 44.1 (C$_{12}$); 51.5 (OCH$_3$).

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