DOI: 10.1002/adsc.200700465

Functional Elastomers *via* Sequential Selective Diene Copolymerization/Hydrophosphorylation Catalysis

Noureddine Ajellal,[a] Erwan Guillevic,[a] Christophe M. Thomas,[a] Ralf Jackstell,[b] Matthias Beller,[b] and Jean-François Carpentier[a,*]

[a] Organométalliques et Catalyse, UMR 6226 CNRS-Université de Rennes 1, 35042, Rennes Cedex, France
Fax: (+33)-2-2323-6939; e-mail: jean-francois.carpentier@univ-rennes1.fr
[b] Leibniz-Institut für Katalyse (LIKAT) an der Universität Rostock e.V., Albert-Einstein-Strasse 29a, 18055, Rostock, Germany

Received: September 21, 2007; Revised: January 10, 2008;

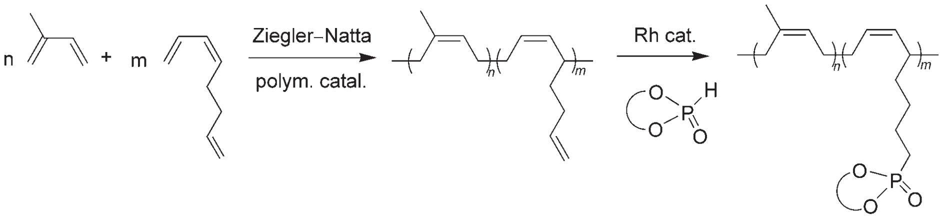
Abstract: An effective preparation of new tailor-made macromolecular materials *via* the combination of two fully atom-efficient catalytic transformations is reported. First, new isoprene-*co*-1,3,7-octatriene [P(IP-*co*-OT)] copolymers with controlled composition (2–21 mol% triene incorporated), molecular weight ($M_n = 23$–$102{,}000\ \mathrm{g\,mol^{-1}}$) and microstructure (1,4-*cis* rich) have been prepared using the homogeneous Ziegler–Natta catalyst system composed of diallylneodymium chloride, magnesium chloride, tetrahydrofuran and methylaluminoxane [$\mathrm{Nd(allyl)_2Cl(MgCl_2)_2(THF)_4/MAO}$]. Next, the pendant vinyl moieties in those P(IP-*co*-OT) copolymers have been selectively transformed into phosphonate groups by hydrophosphorylation in the presence of homogeneous rhodium phosphine catalysts. The latter hydrophosphorylation reaction has been optimized in terms of catalytic activity and selectivity, to define the conditions for an effective and safe procedure that does not affect the macromolecular architecture. All polymer materials have been microstructurally analyzed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, to diagnose the catalyst selectivities in the copolymerization and hydrophosphorylation processes.

Keywords: dienes; homogeneous catalysis; hydrophosphorylation; neodymium; polymerization; rhodium

Introduction

Regio- and stereocontrolled polymers derived from conjugated dienes are of major industrial importance, because of the numerous and large applications of rubber-type materials (tyres, adhesives, etc.).[1] The ultimate properties of polydienes are almost always adjusted by the incorporation of a variety of modifiers and additives.[1] Phosphorylated compounds are very efficient for this purpose and find use in a wide variety of materials, e.g., as flame-retardants. The direct chemical modification of 1,4-polydiene backbones can also modify profoundly some basic properties and allow the preparation of new materials for dedicated applications. In particular, introduction of covalently-bound phosphonate or phosphate functionalities is anticipated to bring anti-oxidizing/corrosive and enhanced adhesive properties on metal surfaces.[2] Surprisingly, there are only few reports on such chemical modifications of 1,4-polydienes.[3] Early attempts were focused on the direct introduction of phosphonate groups *via* radical hydrophosphorylation of polybutadiene chains.[3a] More recently, the grafting of phosphorylated groups along 1,4-polyisoprene chains was investigated *via* the reaction of the P–OH functionality of phosphates or phosphonates with oxirane rings previously created on the polydiene backbone.[3b] However, in both cases, different chemical functionalities were obtained, the microstructure of the final polymers was not defined, and significant degradation or cross-linking of the polymer chains was observed.

In this work, we have envisaged a fundamentally different approach toward such phosphorylated polydienes based on selective, atom-efficient catalysis (Scheme 1). In fact, many rare-earth Ziegler–Natta catalyst systems are known for the controlled polymerization of conjugated dienes.[1,4] In particular, we have recently shown that the simple, readily available binary combination $\mathrm{(allyl)_2NdCl(MgCl_2)_2(THF)_4/MAO}$ (MAO = methylaluminoxane) leads to high catalytic activity and high degree of control for isoprene polymerization, producing up to 98.5% 1,4-*cis*-polymers with number average molecular weights (M_n) in good agreement with calculated values and relatively narrow molecular weights distributions (M_w/M_n).[5] Ziegler–Natta catalysts are also quite effective for co-



Scheme 1. Preparation of phosphorylated elastomers *via* sequential diene copolymerization/hydrophosphorylation catalysis.

polymerizing simple 1,3-dienes (butadiene, isoprene);[6] although, their copolymerization with ω-vinyl-1,3-dienes (e.g., the readily available 1,3,7-octatriene prepared by dimerization of butadiene)[7] is essentially unprecedented in the literature.[8] Such a copolymerization should lead to polydienes with pendant vinyl groups, offering unique opportunities for further chemical functionalization. In a preliminary study,[9] we explored and defined the optimal conditions for the highly effective rhodium-catalyzed hydrophosphorylation[10] of 2-methyl-2,7-octadiene, a model molecular diene that bears one terminal and one trisubstituted C=C bond which mimics a polydiene with pending vinyl groups.

In this article we describe how the latter catalytic developments have been now implemented for preparing 1,4-polydienes bearing pendant phosphonate groups in a highly effective and controlled manner. New isoprene-*co*-1,3,7-octatriene copolymers with controlled composition and microstructure have been first prepared by Ziegler–Natta catalysis and subsequently modified by regioselective Rh-catalyzed hydrophosphorylation of the pending groups (Scheme 1). The molecular structure of the macromolecular chain has been established on the basis of detailed NMR analyses. The thermal properties of the copolymers before and after hydrophosphorylation are also briefly discussed.

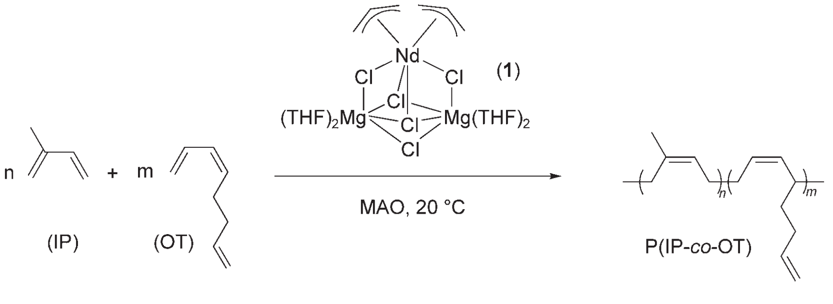
Results and Discussion

Copolymerization of Isoprene and 1,3,7-Octatriene

The copolymerization of isoprene (IP) and 1,3,7-octatriene (OT) was investigated with a catalyst system based on the mixed Nd-Mg complex $(allyl)_2NdCl(MgCl_2)_2(THF)_4$ (**1**) and methylaluminoxane (MAO), using the reaction conditions optimized for the homopolymerization of isoprene (Scheme 2).[5] Catalyst precursor **1** and MAO (30 equiv. *vs.* Nd) were first pre-reacted in toluene at room temperature for 10 min, followed by addition of a hexane solution of isoprene and/or 1,3,7-octatriene at room temperature. Representative results are reported in Table 1.

Preliminary experiments indicated that the homopolymerization of IP (Table 1, entry 1) proceeds significantly faster than that of OT (Table 1, entry 9), with (non-optimized) turnover frequencies (TOFs) of 1120 h^{-1} *vs.* 2 h^{-1}, respectively, under the conditions used. This difference in reactivity can likely be ascribed to the presence of an internal, more sterically hindered C=C bond in OT. Nonetheless, in both cases, good matches between experimental and calculated M_n values, as well as relatively narrow molecular weight distributions, were observed. These data establish that the high degree of control over the polymerization previously evidenced for isoprene pertains in the case of the 1,3,7-octatriene.

Copolymerization experiments were performed using variable ratios of the 1,3-diene and 1,3,7-triene. As a consequence of the relatively slow polymerization rate of OT, the more OT in the feed, the



Scheme 2. Preparation of 1,4-polydienes with pendant vinyl groups *via* copolymerization of isoprene and 1,3,7-octatriene.

Table 1. Copolymerization of isoprene (IP) and 1,3,7-octatriene (OT).[a]

Entry	IP [mmol]	OT [mol%]	[IP+OT]/ [Nd]	Vinyl[b] [mol%]	Time[c] [h]	Yield[d] [%]	$M_n^{calcd.[e]}$ $[10^{-3}]$	$M_n^{exp[f]}$ $[10^{-3}]$	$M_w/M_n^{[f]}$	T_g [°C]
1	20.1	0	1180	0	1	95	73	78	1.73	−61.8
2	20.4	5.5	1270	2.0	20	85	77	83	1.93	−58.7
3	12.9	10.4	845	5.5	53	88	51	61	1.63	−61.1
4	25.9	10.4	1700	5.7	53	86	102	110	1.83	−58.4
5	17.0	20.5	1253	9.2	48	83	75	96	1.98	nd
6	9.7	23.0	741	11.0	48	82	34	54	1.44	−55.1
7	4.5	30.7	382	12.5	70	76	23	17	1.77	−49.3
8	3.7	54.0	476	21.0	72	63	42	37	2.10	−43.9
9	0	100	235	100.0	45	49	12	16	2.06	nd

[a] $Nd(allyl)_2Cl(MgCl_2)_2(THF)_4 = 17$ µmol; [Al]/[Nd] = 30; toluene/hexane = 5 + 3 mL; activation time = 10 min; polymerization carried out at 20 °C; the results shown for each entry are representative of at least two reproducible (±5%) runs.

[b] Comonomer content determined by ^{1}H NMR in $CDCl_3$.

[c] Polymerization time (not optimized).

[d] Isolated yield of (co)polymer.

[e] Average number molecular weight in g.mol^{-1} calculated from the relation: [IP + OT]/[Nd] × yield [%] × [(OT mol% × 108)] + [(IP mol% × 68)].

[f] Average number molecular weight in gmol^{-1} and polydispersity determined by GPC *vs.* PS standards.

slower was the polymerization (Table 1, entries 2–8). Also, in all cases, we observed that only *ca.* 50% of OT engaged is converted and actually incorporated in the copolymer (*vide infra*). GPC analyses evidenced that only true P(IP-*co*-OT) copolymers with monodisperse distributions are produced; i.e., homopolymers of IP and OT were not detectable. In fact, Figure 1 and Figure 2 show that the monomodal GPC trace of a typical P(IP-*co*-OT) copolymer that contains 9.2 mol% of triene (Table 1, entry 5) does not superimpose with either the monomodal trace of homoPOT prepared using a similar [OT]/[Nd] loading ([OT]/[Nd] = 235; entry 9) or with the bimodal GPC trace of a mixture of PIP and POT homopolymers prepared under similar conditions (entries 1 and 9, respectively). Further confirmation of the formation of true P(IP-*co*-OT) copolymers is also obtained after hydrophosphorylation has been carried out (*vide infra*).

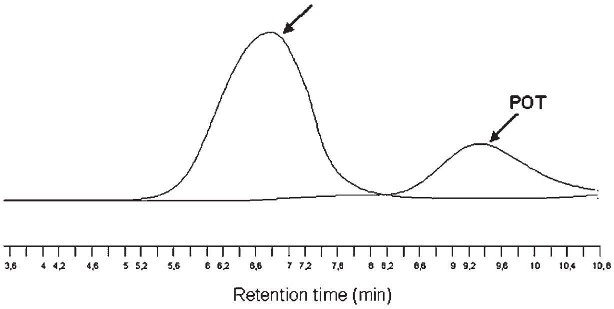


Figure 1. GPC traces (THF, 20 °C, RI detection) of P(IP-*co*-OT) copolymer (Table 1, entry 5) and homoPOT (Table 1, entry 9).

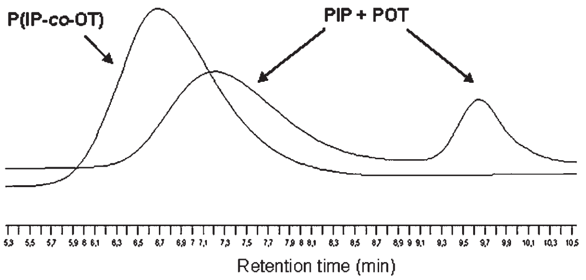


Figure 2. GPC traces (THF, 20 °C, RI detection) of P(IP-*co*-OT) copolymer (Table 1, entry 5) and a mixture of homopolymers PIP (Table 1, entry 1) + POT (Table 1, entry 9).

More, the experimental M_n values of these copolymers match well again the calculated ones (see Table 1). Considering this difference in reactivity but overall good control, it turned out to be possible to prepare, with good yields, copolymers with on demand defined molecular weights and contents of OT, that is, pendant vinyl units, in the range 2–21 mol%, by adjusting the monomer-to-catalyst and IP-to-OT ratios. For instance, doubling the monomer-to-catalyst ratio, keeping constant the OT content of 10.4 mol% in the feed, allowed the preparation of two copolymers with approximately the same amount of incorporated triene (5.5–5.7 mol%), similar polydispersity ($M_w/M_n = 1.6$–1.8), and nearly doubled molecular weights (Table 1, entries 3 and 4).

The obtained copolymers were characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy (Figure 3, Figure 4 and Figure 5). The OT content in the copolymers was readily determined by ^{1}H NMR, from the relative integration between the pendant vinyl hydrogens ($\delta =$ 5.6–5.9 ppm) and the singlet resonance for the meth-

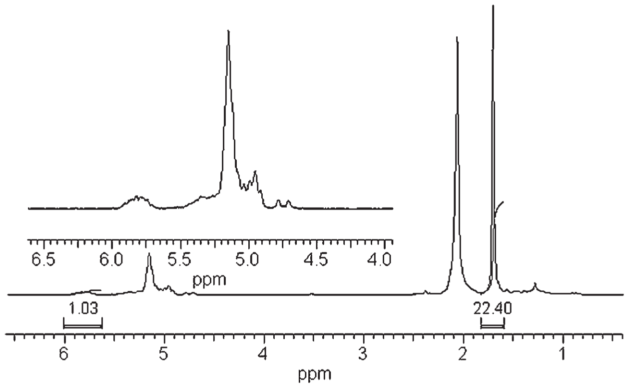


Figure 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 20 °C) of a P(IP-*co*-OT) copolymer containing 11.0 mol% of triene (Table 1, entry 6).

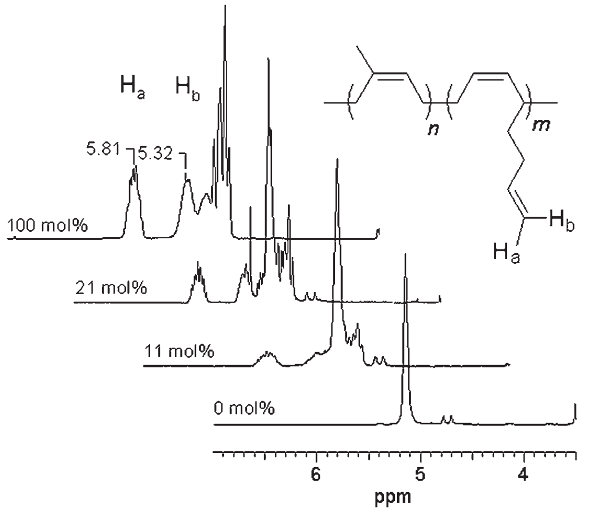


Figure 4. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 20 °C) of P(IP-*co*-OT) copolymers with varying OT contents.

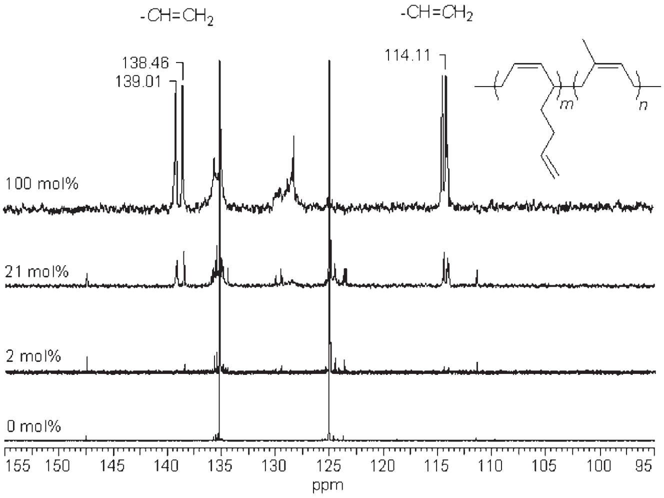


Figure 5. Details of the $^{13}C\{^1H\}$ NMR spectra (75 MHz, $CDCl_3$, 20 °C) of P(IP-*co*-OT) copolymers with varying OT contents.

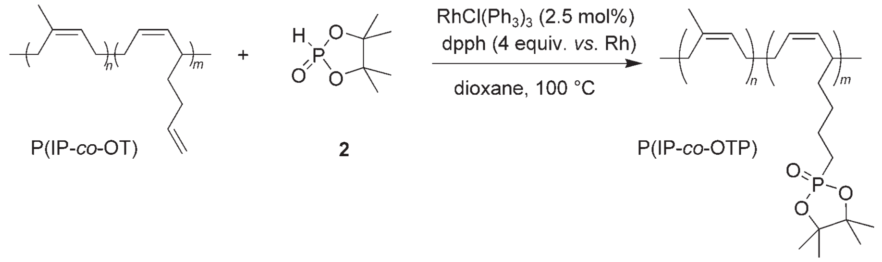
ylene hydrogens of 1,4-*cis*-polyisoprene ($\delta =$ 1.67 ppm) (Figure 3 and Figure 4). In fact, NMR data show that the polyisoprene backbone in those P(IP-*co*-OT) copolymers retains a high (> 95%) 1,4-*cis* stereoselectivity [exact determination of the stereoselectivity of the whole polydiene backbone is complicated by the presence of octatriene units, which induce additional resonances for block junctions], as observed for homopolyisoprenes prepared under similar conditions.[5] The ^{13}C NMR spectra of the copolymers contain, in addition to the signals for *cis*-polyisoprene units, well-defined vinyl signals at $\delta = 138.46$ and 139.01 (=*C*H) and $\delta = 114.11$ and 114.45 (=*C*H_2) ppm (Figure 5) [the observation of two sets of signals, of similar intensity, for pendant vinyl units (Figure 5) likely reflects the absence of regioselectivity for octatriene and isoprene enchainments, that is, the presence of head-to-tail and head-to-head junctions].

The glass transition temperatures (T_g) of the prepared polymers were determined by differential scanning calorimetry (DSC). As expected, an increase of the T_g values with the OT content was observed, from *ca.* −62 °C for 1,4-*cis*-polyisoprene up to *ca.* −44 °C when 21 mol% of 1,3,7-octatriene was copolymerized. When up to 5 mol% of OT copolymerized, the impact on T_g was less sensitive, that is, the elastomeric properties of 1,4-*cis*-polyisoprene are not significantly affected.

Catalytic Hydrophosphorylation of P(IP-*co*-OT) Copolymers

Our preliminary model study showed that hydrophosphorylation of 7-methyl-1,6-octadiene with the cyclic pinacol-based phosphonate **2** in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ modified by the bidentate ligand 1,6-bis(diphenylphoshino)hexane (dpph) proceeds under mild conditions with high productivity and activity, and high selectivity as well.[9] In fact, the linear (*anti*-Markovnikov) hydrophosphorylation product of the vinyl bond was the only product observed under these conditions; i.e., the catalyst system operates *via* steric discrimination between internal (substituted) and terminal olefins. This result suggested us that internal C=C bonds such as those present in polyisoprene/polyoctatriene backbones should not be affected. The hydrophosphorylation of P(IP-*co*-OT) copolymers was therefore investigated under such conditions (Scheme 3). Representative results obtained at 100 °C with 2.5 mol% loading of Rh catalyst *vs.* pending vinyl functions are summarized in Table 2.

A preliminary control experiment performed with 1,4-*cis*-homopolyisoprene (using 2.5 mol% of Rh *vs.* internal C=C bonds) (Table 2, entry 1) confirmed that (i) no hydrophosphorylation takes place on the poly-



Scheme 3. Rh-catalyzed hydrophosphorylation of P(IP-*co*-OT) copolymers.

Table 2. Rh-catalyzed hydrophosphorylation of isoprene-*co*-1,3,7-octatriene copolymers.[a]

Entry	Vinyl[b] [mol%]	Time [h]	[**2**]/[vinyl]	Conversion[c] [%]	M_n(i)[d] [10^{-3}]	M_n(f)[e] [10^{-3}]	M_w/ M_n(i)[d]	M_w/ M_n(f)[e]	T$_g$ [°C]
1[f,g]	0	42	0.6[f]	0	98	98	1.73	1.76	−61.8
2[h]	2.0	72	1.0	50	83	94	2.00	2.05	nd
3[h]	2.0	41	3.0	79	83	71	1.93	2.10	−55.2
4	2.0	64	3.0	>99	83	102	1.93	1.92	−53.7
5	5.5	70	3.0	94	61	56	1.63	1.70	−57.2
6	5.7	70	3.0	92	110	98	1.84	1.80	−52.2
7	9.2	23	3.0	92	96	85	1.98	1.90	nd
8[i]	9.2	35	3.0	72	96	90	1.98	1.95	nd
9[i]	5.7	7	3.0	91	110	108	1.98	1.91	nd
10[k]	5.7	3	3.0	89	110	44	1.98	2.85	nd
11	11.0	40	3.0	92	54	46	1.44	1.50	−53.6
12	12.5	70	3.0	95	17	nd	1.77	nd	nd
13	21.0	40	3.0	86	37	27	2.10	1.90	−34.0
14	100.0	75	3.0	>99	16	11	2.06	1.78	−8.1

[a] Vinyl/dpph/RhCl(PPh$_3$)$_3$ = 40:4:1, T = 100 °C, [polymer] = 1.2×10^{-3} M in toluene.
[b] OT content in the copolymer, as determined by ^{1}H NMR.
[c] Determined by ^{1}H NMR and ^{13}C NMR in CDCl$_3$.
[d] Average number molecular weight in g mol^{-1} and polydispersity determined by GPC before hydrophosphorylation.
[e] Determined by GPC after hydrophosphorylation.
[f] Hydrophosphorylation of 1,4-*cis*-polyisoprene using 2.5 mol% Rh *vs.* internal C=C bonds.
[g] Dioxane used as solvent.
[h] PPh$_3$ (4 equiv.) instead of dpph.
[i] T = 120 °C, solvent = diglyme.
[k] T = 140 °C, solvent = diglyme.

diene backbone (^{31}P NMR), (ii) the cyclic phosphonate **2** is not consumed by side processes (^{31}P NMR), and (iii) the polydiene chains are not degraded under the chosen reaction conditions (^{1}H NMR, GPC). Thus, expectedly, the reactions of copolymers (Table 2, entries 2–13) led to a single product, that is the linear hydrophosphorylation product of the pendant vinyl functions, as identified by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy (Figure 6). The most noticeable NMR features include the appearance of two major singlet resonances in the ^{31}P{^{1}H} NMR spectrum at $\delta = 45.44$ and 45.56 ppm (*vs.* 17.06 ppm for **2**) [the observation of two close ^{31}P NMR signals of similar intensity is to be related to the two sets of signals observed for the pendant vinyl groups, which is assumed to arise from head-to-tail/head-to-head regioisomers (see above)], and the disappearance of the vinyl resonances in the ^{13}C{^{1}H} along the appearance of a singlet at $\delta = 87.70$ ppm (*vs.* 88.90 ppm for **2**) for the pinacol phosphonate group.

Following the conditions optimized for the hydrophosphorylation of the model molecular substrate,[9] initial experiments with P(IP-*co*-OT) copolymers were conducted using 1,4-dioxane as the solvent (Table 2, entries 2 and 3). However, moderate conversions of the vinyl functions were observed in these conditions, even in the presence of an excess of **2**, a phenomenon which is assumed to arise from the poor solubility of the copolymers in this solvent at 100 °C. Toluene proved to be much more efficient as solvent, leading to high conversions (86–100%) for a set of copolymers with various vinyl (OT) contents (2–21 mol%), as well as an homopoly(1,3,7-octatriene) (Table 2, entries 4–7, and 11–14). In line with the re-

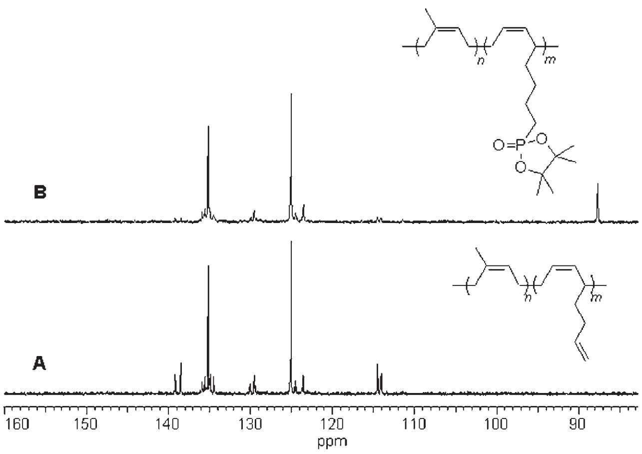


Figure 6. Details of the $^{13}C\{^1H\}$ NMR spectra (75 MHz, $CDCl_3$, 20 °C) of P(IP-*co*-OT) copolymers with 21 mol% OT content: **A**: Initial vinyl polymer (Table 1, entry 8), **B**: a 86% phosphorylated polymer (Table 2, entry 13).

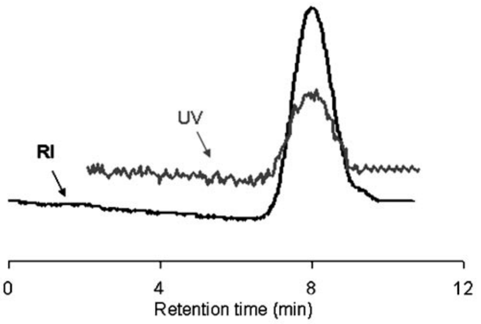


Figure 7. GPC traces (THF, 20 °C) with double detection RI/UV (254 nm) of a phosphorylated P(IP-*co*-OT) copolymer with 21 mol% OT content (Table 2, entry 13).

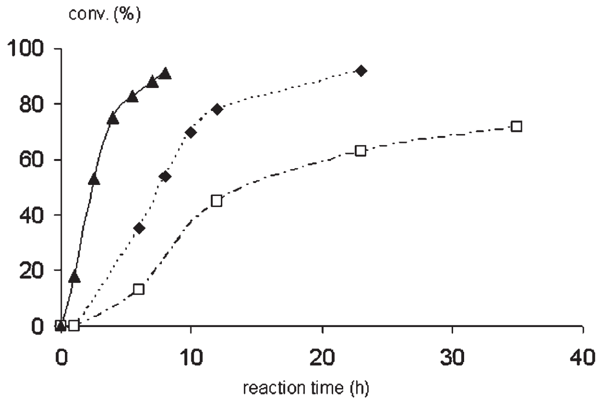


Figure 8. Kinetics of the hydrophosphorylation of a isoprene-*co*-1,3,7-octatriene copolymer with phosphonate **2** promoted by $[RhCl(PPh_3)_3]$/phosphine systems ([**2**]/[vinyl]/[phosphine]/[Rh] = 120:40:4:1. ▲ dpph (120 °C, diglyme, Table 2, entry 9), ◆ dpph (100 °C, toluene, Table 2, entry 7), □ PPh_3 (100 °C, toluene, Table 2, entry 8).

sults observed on the model substrate, catalyst systems based on triphenylphosphine instead of dpph were found to be significantly less active (Table 2, entry 8, Figure 8).

At 100 °C, in all cases, we observed that the molecular weight distributions (M_w/M_n) did not change after the hydrophosphorylation was performed. Also, the number average molecular weights of the final hydrophosphorylated polymers were similar or somewhat lower as compared to those of the initial vinyl polymers, a small variation which can be accounted for by the modification of the hydrodynamic volume of the copolymers. These observations attest that the catalytic approach used for hydrophosphorylation is a safe procedure that does not significantly affect the macromolecular architecture. Analysis of a representative hydrophosphorylated copolymer (Table 2, entry 13) by GPC using dual UV/RI detection showed that the phosphonate functionality (selectively detected by UV at 254 nm) is equally distributed over the whole polymer distribution (detected by RI) (Figure 7). This observation further confirms the formation of true P(IP-*co*-OT) copolymers; actually, if a mixture of homopolymers (i.e., POT and PIP) would be formed, the phosphonate functionality would be selectively introduced onto POT (as PIP is not affected by hydrophosphorylation) and would appear only at low molecular weights in the GPC-UV trace.

When the reaction temperature was increased up to 120 °C (using diglyme as the solvent), a marked increase in the reaction kinetics was observed (Figure 8), allowing completion of the hydrophosphorylation within shorter time periods while still recovering an undamaged phosphorylated polymer (Table 2, entry 9). On the other hand, significant decomposition of the polymer was observed when the reaction was conducted at 140 °C, as evidenced by the decreased M_n value and the broadened molecular weight distribution (Table 2, entry 10).

Conclusions

In conclusion, we have set up an effective preparation of new tailor-made phosphorylated polymers *via* the combination of two fully atom-efficient catalytic transformations. For the first time isoprene-*co*-1,3,7-octatriene copolymers with controlled composition and microstructure were prepared using homogeneous Ziegler–Natta catalysis. The pendant vinyl moieties in those P(IP-*co*-OT) copolymers can be easily transformed into phosphonate groups by hydrophosphorylation in the presence of homogeneous Rh-phosphine catalysts. The hydrophosphorylation takes place selectively at the terminal alkene function and appears to be a safe procedure that does not affect the macromolecular architecture. Similar approaches towards original macromolecular materials that combine discrete homogeneous catalysts are underway in our laboratories and will be reported in due course.

Experimental Section

General Conditions

All manipulations requiring dry atmosphere were performed under purified argon by use of standard Schlenk techniques or in a glove box. Solvents (toluene, hexane, 1,4-dioxane, diglyme) were distilled from sodium-benzophenone ketyl under argon, stored under argon and degassed by freeze-thaw-vacuum cycles prior to use. Isoprene (Aldrich, 99.98%) was distilled twice from CaH_2, stored under argon and degassed by freeze-thaw-vacuum cycles prior to use. 1,3,7-Octatriene,[7] complex $(allyl)_2NdCl(MgCl_2)_2(THF)_4$ (**1**),[5] and cyclic phosphonate **2**[11] were prepared according to literature procedures. MAO (Albermale, 30 wt% solution in toluene) was used as received. Phosphine ligands (dpph, PPh_3,) and $RhCl(PPh_3)_3$ were purchased from Aldrich and used as received.

NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers at ambient probe temperature. ^1H (200 and 300 MHz) and ^{13}C (75 MHz) chemical shifts are reported in ppm *vs.* $SiMe_4$ and were determined by reference to the residual solvent peaks. $^{31}P\{^1H\}$ chemical shifts were referenced to external H_3PO_4. Gel permeation chromatography (GPC) was performed using THF as solvent (1 mL min^{-1}) at 20 °C on a Waters 600 instrument equipped with combined UV/RI detectors, or a Polymer Laboratories PL-GPC 50 plus apparatus (PLgel 5 μm MIXED-C 300 × 7.5 mm, equipped with combined RI and dual angle LS (PL-LS 45/90°) detectors. Polyisoprene molecular weights were determined *vs.* polystyrene standards. DSC measurements were performed on a TA Instruments DSC 2920 differential scanning calorimeter.

Copolymerization of Isoprene with 1,3–7-Octatriene

A typical polymerization is as follows (Table 1, entry 4). In the glove box, a Schlenk flask containing a magnetic stir bar was charged with the catalyst precursor **1** (12.3 mg, 17.0 μmol) and the appropriate amount of MAO (100 mg of a 30 wt% solution in toluene, 0.51 mmol) in toluene (5.0 mL) was transferred in by syringe. The mixture was stirred at room temperature for 10 min, and a solution of isoprene (1.76 g, 25.9 mmol) and 1,3,7-octatriene (325.1 mg, 3.01 mmol) in hexane (3.0 mL) was added under vigorous stirring. After the desired polymerization time, the reaction was quenched by adding a methanol solution acidified with 10% HCl (*ca.* 1 mL), and methanol (*ca.* 10 mL) was further added. The supernatant liquids were removed by pipette; the polymer was washed with methanol and dried under vacuum at 40 °C for 8 h; yield: 1.79 g (86%).

Catalytic Hydrophosphorylation of Poly(isoprene-*co*-1,3,7-octatriene) Copolymers with Pinacol Phosphonate 2

In a typical procedure (Table 2, entry 7), a Schlenk flask containing a magnetic stir bar was charged with a P(IP-*co*-OT) copolymer (Table 1, entry 12) (67 mg, 0.115 mmol OT), phosphonate **2** (56.6 mg, 0.345 mmol), $RhCl(PPh_3)_3$ (2.7 mg, 2.88 μmol), dpph (5.2 mg, 11.5 μmol) and toluene (1.5 mL). The mixture was stirred in an oil bath at 100 °C. Small aliquots were periodically sampled and subjected to ^1H and $^{31}P\{^1H\}$ NMR for determining the conversion. After the desired reaction time, the mixture was cooled to room temperature, solvents were removed under vacuum, and the copolymer was precipitated by adding a 1:1 mixture of ethyl acetate/Et_2O (*ca.* 3 mL). The supernatant liquids were removed; the polymer was washed with methanol and dried under vacuum at 40 °C for 8 h; yield: 62.3 mg (93%).

Acknowledgements

This work was generously supported by the CNRS and Institut Universitaire de France (IUF).

References

[1] For reviews, see: a) L. Porri, A. Giarrusso, in: *Comprehensive Polymer Science*, (Eds.: G. C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt), Pergamon Press, Oxford, **1989**, Vol. 4, pp 53–108; b) R. Taube, G. Sylvester, in: *Applied Homogeneous Catalysis*, (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, Vol. 1, pp 280–318.

[2] a) J. C. Brosse, I. Campistron, D. Derouet, A. El Hamdaoui, D. Reyx, S. Ritoit-Gillier, *J. Appl. Polym. Sci.* **2000**, *78*, 1461; b) W. El Khatib, B. Youssef, C. Bunel, B. Mortaigne, *Polym. Int.* **2003**, *52*, 146, and references cited therein.

[3] a) E. E. Nifant'ev, A. I. Kapralov, R. K. Magdeeva, Y. L. Chichagova, I. V. Razumovskaya, *Vysokomol. Soedin., Ser. A* **1983**, *25*, 404; *Chem. Abst.* **1983**, 144770; b) D. Derouet, J.-C. Brosse, L. Cauret, F. Morvan, S. Mulder-Houdayer, *J. Appl. Polym. Sci.* **2003**, *87*, 47.

[4] Selected reviews: a) Z. Shen, J. Ouyang, in: *Handbook on the Physics and Chemistry of Rare Earth Metals*, (Eds.: K. A. Gschneidner, Jr., L. Fleming), Elsevier, Dordrecht, **1987**, chap. 61; b) L. Friebe, O. Nuyken, W. Obrecht *Adv. Polym. Sci.* **2006**, *204*, 1.

[5] N. Ajellal, L. Furlan, C. M. Thomas, O. Casagrande Jr, J.-F. Carpentier, *Macromol. Rapid Commun.* **2006**, *27*, 338.

[6] a) L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, *Angew. Chem.* **2007**, *119*, 1941; *Angew. Chem. Int. Ed.* **2007**, *46*, 1909; b) S. Kaita, Y. Doi, K. Kaneko, A. C. Horiuchi, Y. Wakatsuki, *Macromolecules* **2004**, *37*, 5860; c) A. Oehme, U. Gebauer, K. Gehrke, P. Beyer, B. Hartmann, M. D. Lechner, *Macromol. Chem. Phys.* **1994**, *195*, 3773.

[7] S. Harkal, R. Jackstell, F. Nierlich, D. Ortmann, M. Beller, *Org. Lett.* **2005**, *7*, 541.

[8] For the copolymerization of butadiene/isoprene with α,ω-dienes (1,5-hexadiene, 1,7-octadiene), see: F. Bonnet, M. Visseaux, D. Barbier-Baudry, A. Dormond, *Macromolecules* **2002**, *35*, 1143.

[9] N. Ajellal, C. M. Thomas, J.-F. Carpentier, *Adv. Synth. Catal.* **2006**, *348*, 1093.

[10] For catalytic hydrophosphorylation, see: a) L.-B. Han, C.-Q. Zhao, M. Tanaka, *J. Org. Chem.* **2001**, *66*, 5929; b) L.-B. Han, R. Hua, M. Tanaka, *Angew. Chem.* **1998**, *110*, 98; *Angew. Chem. Int. Ed.* **1998**, *37*, 94; c) L.-B. Han, N. R. Choi, M. Tanaka, *Organometallics* **1996**, *15*, 3259; d) C.-Q. Zhao, L.-B. Han, M. Goto, M. Tanaka, *Angew. Chem.* **2001**, *113*, 1983; *Angew. Chem. Int. Ed.* **2001**, *40*, 1929; e) L.-B. Han, F. Mirzaei, C.-Q. Zhao, M. Tanaka, *J. Am. Chem. Soc.* **2000**, *122*, 5407; f) J. F. Reichwein, M. C. Patel, B. L. Pagenkopf, *Org. Lett.* **2001**, *3*, 4303; g) M. O. Shulyupin, G. Franciò, I. P. Beletskaya, W. Leitner, *Adv. Synth. Catal.* **2005**, *347*, 667.

[11] A. Munoz, C. Hubert, J.-L. Luche, *J. Org. Chem.* **1996**, *61*, 6015.