

Polymer Communication

# Functionalization of polybutadiene by rhodium(I)-catalyzed coupling with 2-vinylpyridines: introduction of pyridyl groups to phenyl-terminated polybutadiene

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Received 19 June 1999; received in revised form 23 August 1999; accepted 27 August 1999

## Abstract

Vinyl groups in phenyl-terminated polybutadienes **1–3**, 99% unsaturated, were functionalized with 2-isopropenylpyridine (IPP, 1 equiv.) in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  (10 mol%). The resulted polymers had about 50% of conversion ratio of 1,2-units of the original polymers. Also, PTPBs **4–5**, 60% unsaturated, gave about 45% of conversion ratio in vinyl groups under the same reaction conditions. By using the substrate with several gave 45, 28, 15 and 6% of conversion ratios in the vinyl groups, respectively. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Polybutadiene; Coupling reaction; Rhodium catalyst

## 1. Introduction

The catalytic functionalization of an unsaturated polymer by transition metal complex is one of the most interesting fields for the synthesis of special polymers containing desirable functional groups [1]. Of polymers, polybutadiene is a good substrate for this purpose because it is easily available, in various ranges of molecular weight, with different degrees of unsaturation.

Recently, we have found that the cross-coupling reaction of 2-vinylpyridines and 2-phenylpyridines with terminal olefins in the presence of a rhodium(I) catalyst to give the alkylated products (Scheme 1) [2–7]. To our knowledge, the application of this coupling reaction to an unsaturated polymer has not been reported. In particular, the modified polymer containing pyridine rings has feasibility as a polymer for drug delivery systems [8] and polymer-bound ligands [9]. So we decided that phenyl-terminated polybutadienes (PTPBs) are applied instead of terminal olefin to this type of coupling reaction. Here we report the preliminary results of the functionalization of PTPBs with 2-isopropenylpyridine (IPP) by the Wilkinson complex,  $\text{RhCl}(\text{PPh}_3)_3$ .

## 2. Experiment

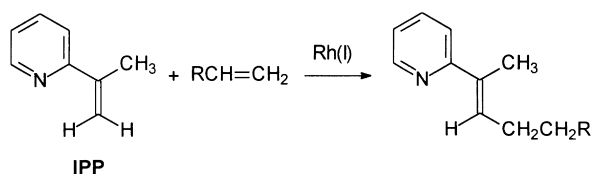
### 2.1. Materials

All polymers **1–5** used in this reaction were purchased from Aldrich Chem Co. and used without further purification: **1**, 99% unsaturated, 40% vinyl, 30% *trans*-1,4,  $M_n$  1300; **2**, 99% unsaturated, 25% vinyl, 40% *trans*-1,4,  $M_n$  1500; **3**, 99% unsaturated, 25% vinyl, 40% *trans*-1,4,  $M_n$  3400; **4**, 60% unsaturated, 45% vinyl, 10% *trans*-1,4, 5% *cis*-1,4,  $M_n$  1000; **5**, 60% unsaturated, 45% vinyl, 10% *trans*-1,4, 5% *cis*-1,4,  $M_n$  1800. The Wilkinson catalyst,  $\text{RhCl}(\text{PPh}_3)_3$  and aluminum oxide (neutral, Brockmann I, 150 mesh) were purchased from Aldrich Chem Co. 2-Isopropenylpyridine (IPP) was prepared as described in the literature [10]. Toluene was refluxed and then distilled over calcium hydride prior to use.

### 2.2. Equipment and analytical measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC-300F spectrometer. The chemical shifts are reported in ppm relative to internal tetramethylsilane in  $\text{CDCl}_3$  for  $^1\text{H}$  NMR and signals of  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR, respectively. The conversion ratios were determined from the ratio of vinyl protons' integral of polymer functionalized to vinyl protons' integral of original polymers in  $^1\text{H}$  NMR spectra. Infrared

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(IR) spectra were recorded using a Bruker IFS 88 instrument.

### 2.3. Reactions

The following is an example of a typical experimental procedure: a screw-capped vial (5 ml) was charged with 64.3 mg of **1** ( $M_n$  1300, 99% unsaturated), 50 mg (0.326 mmol, 1 equiv.) of IPP, and 38.8 mg (10 mol% based on IPP) of the Wilkinson complex in toluene (3 ml). The reaction mixture was heated at 130°C for 24 h with stirring. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on aluminum oxide (hexane:EtOAc = 5:2) to give 83 mg (94% yield based on the polymer; conversion ratio of the vinyl group was 48%).

### 3. Results and discussion

In our study, PTPBs were used: PTPBs **1** (99% unsaturated,  $M_n$  1300 containing 40% of vinyl groups); **2** (99% unsaturated, 25% vinyl, 40% *trans*-1,4,  $M_n$  1500); **3** (99% unsaturation, 25% vinyl, 40% *trans*-1,4,  $M_n$  3400); **4** (60% unsaturation, 45% vinyl, 10% *trans*-1,4, 5% *cis*-1,4,  $M_n$  1000); and **5** (60% unsaturation, 45% vinyl, 10% *trans*-1,4, 5% *cis*-1,4,  $M_n$  1800).

The coupling reaction of PTPBs **1–3** with IPP was carried out according to Scheme 2. PTPB **1** reacted with IPP

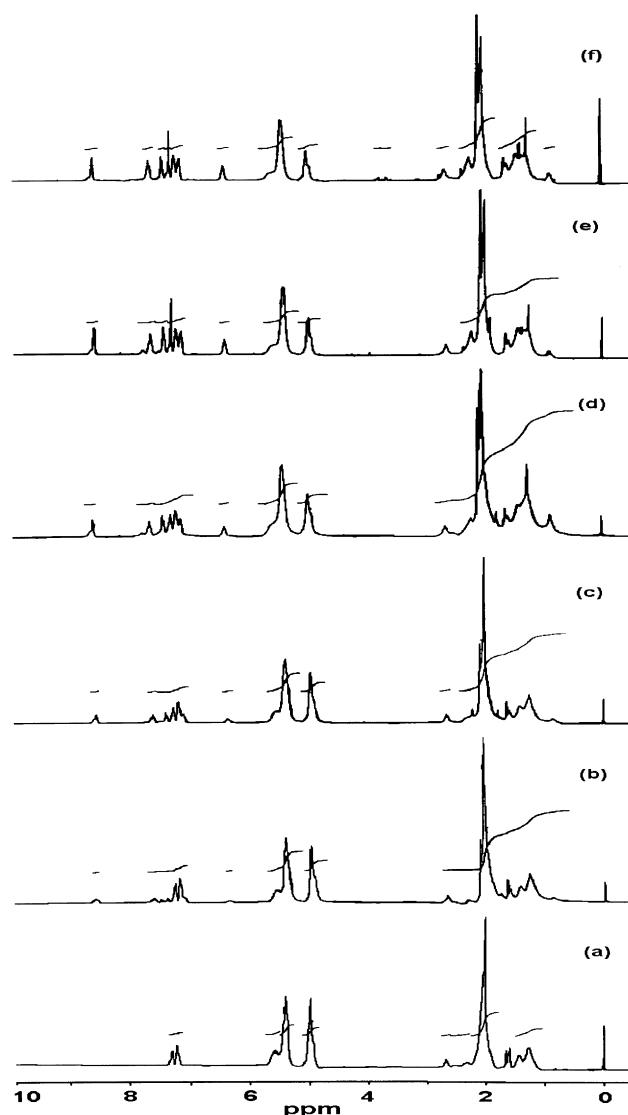
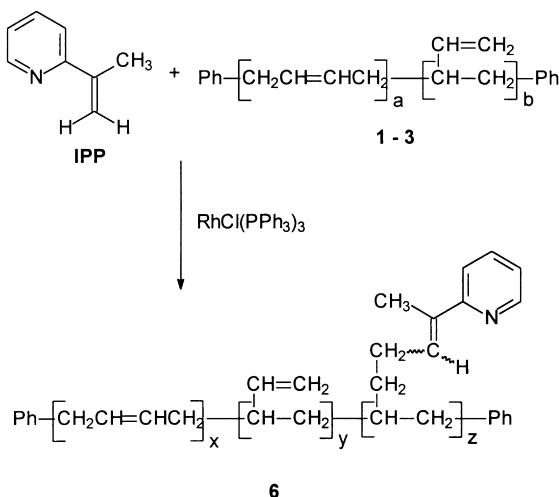
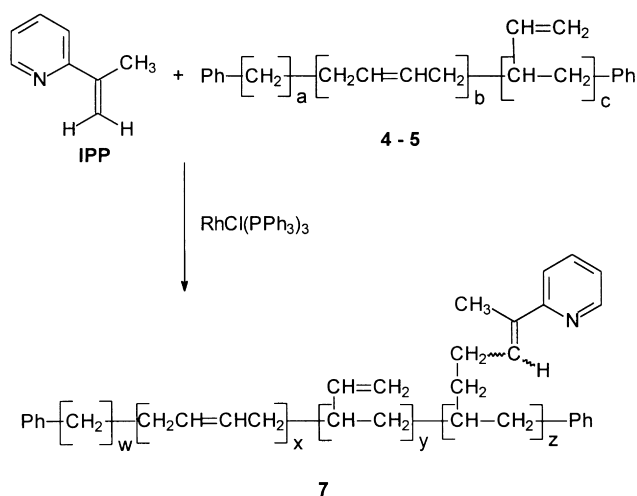


Fig. 1.  $^1\text{H}$  NMR spectra of **1** (a) and functionalized (b)–(f) polymers ((b) **6g**, conversion, 6%; (c) **6f**, conversion, 15%; (d) **6e**, conversion, 28%; (e) **6d**, conversion, 45% (f) **6a**, conversion, 48%).

(1 equiv. to vinyl group) in the presence of the Wilkinson complex (10 mol%) in toluene at 130°C for 24 h to give the desired coupled polymer **6a** having 48% of conversion ratio in the vinyl groups of **1** after chromatographic purification. The resulted polymer **6a** changed to less soluble and more viscose polymer than the original polymer.

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and IR spectra provide convincing evidence for real coupling of the polymer. In  $^1\text{H}$  NMR new signals of the protons of the pyridine ring appear at the region 7.2–8.6 ppm and the vinylic signal of the original polymer **1** significantly lowered. To obtain the functionalized polybutadienes having various content of the pyridine moiety, different ratios of substrate (0.8, 0.6, 0.43 and 0.27 equiv.) based on **1** were applied (runs 4–7 of Table 1). These reactions gave 45, 28, 15 and 6% of conversion ratio in the vinyl moiety, respectively. As amounts of



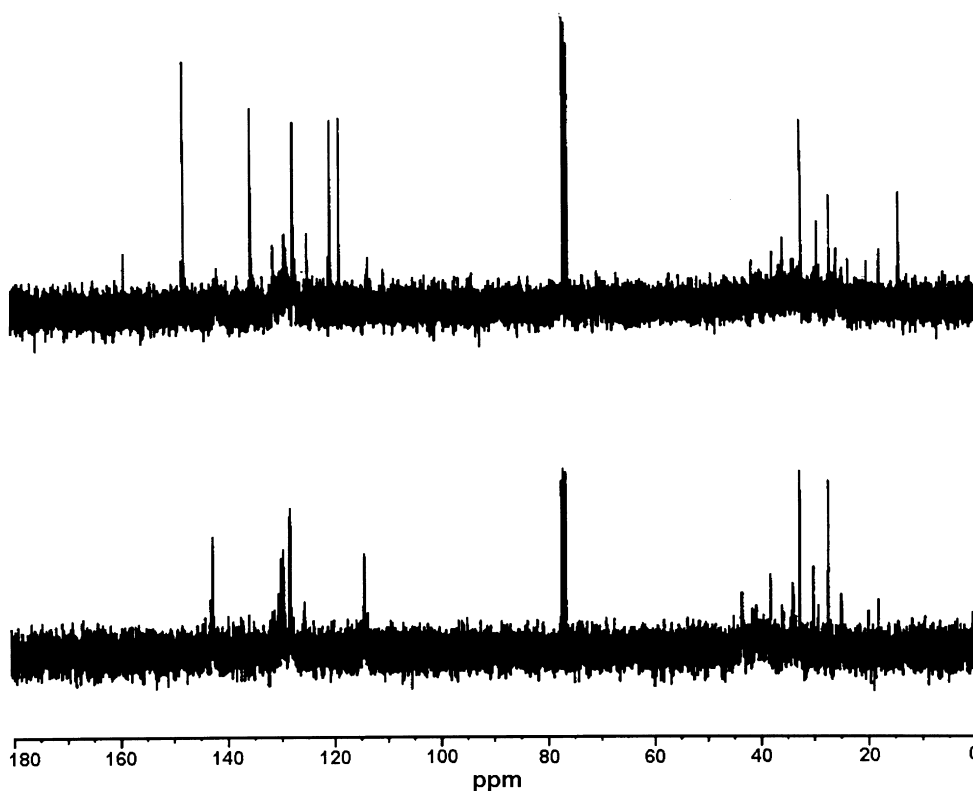
Scheme 3.

substrate based on **1** were used, various polymers having different conversion ratios could be obtained. The tendency of the vinylic signal according to conversion ratio is shown in Fig. 1. In  $^{13}\text{C}$  NMR, while the signals of vinyl carbons at 142.6 and 114.4 in **1** marked lowered, the polymer has new signals at 160.0, 148.7, 136.1, 121.2, 119.5 and 14.2 ppm; these signals are the specific signals [6] of the carbons of the pyridine ring and carbons of the methyl group (see Fig. 2). In the IR spectrum of the initial PTPB **1**, a medium band at

$1639\text{ cm}^{-1}$  due to stretching vibration of  $\text{C}=\text{C}$  of vinyl groups and a medium band at  $3074$  assigned to stretching vibrations of  $=\text{C}-\text{H}$  bond as well as a strong band at  $910$  and  $967\text{ cm}^{-1}$  characteristic of deformation vibrations of  $=\text{C}-\text{H}$  bonds, were observed. After functionalization of **1** by its treatment with IPP, all these bands were markedly lowered. Moreover, the spectra reveal a presence of new bands at  $1584$ ,  $775$  and  $742\text{ cm}^{-1}$  attributable to the pyridine rings (Fig. 3). The IR spectra according to conversion ratio are shown in Fig. 3. In order to obtain higher conversion ratio, use of excess of IPP (2 equiv.) or longer reaction time (48 h) were applied to this coupling reaction. Longer reaction time, however, gave increased conversion slightly to 50% (run 2 of Table 1). Excess of IPP gave lower conversion ratio (21%) unexpectedly (run 3 of Table 1). It may be due to the stabilization of rhodium complex by excess of IPP as ligands.

2-Vinylpyridine, commercially available substrate, reacted with **1** but the desired polymer was not obtained unfortunately, because of its low reactivity [6].

Other PTPBs applied to this coupling reaction. The results of the coupling reaction are listed in Table 2. Polymers (99% unsaturated) **2** and **3** gave the desired products **6h-i** having 52 and 50% of conversion ratios under the same reaction conditions, respectively (runs 1 and 2 of Table 2). Polymers (60% unsaturated) **4** and **5** also worked well and gave **7a-b** having 45 and 43% of conversion ratios under the same reaction conditions, respectively, as shown in Scheme 3 (runs 3 and 4 of Table 2).

Fig. 2.  $^{13}\text{C}$  NMR spectra of **1** (bottom) and functionalized polymer **6a** (top).

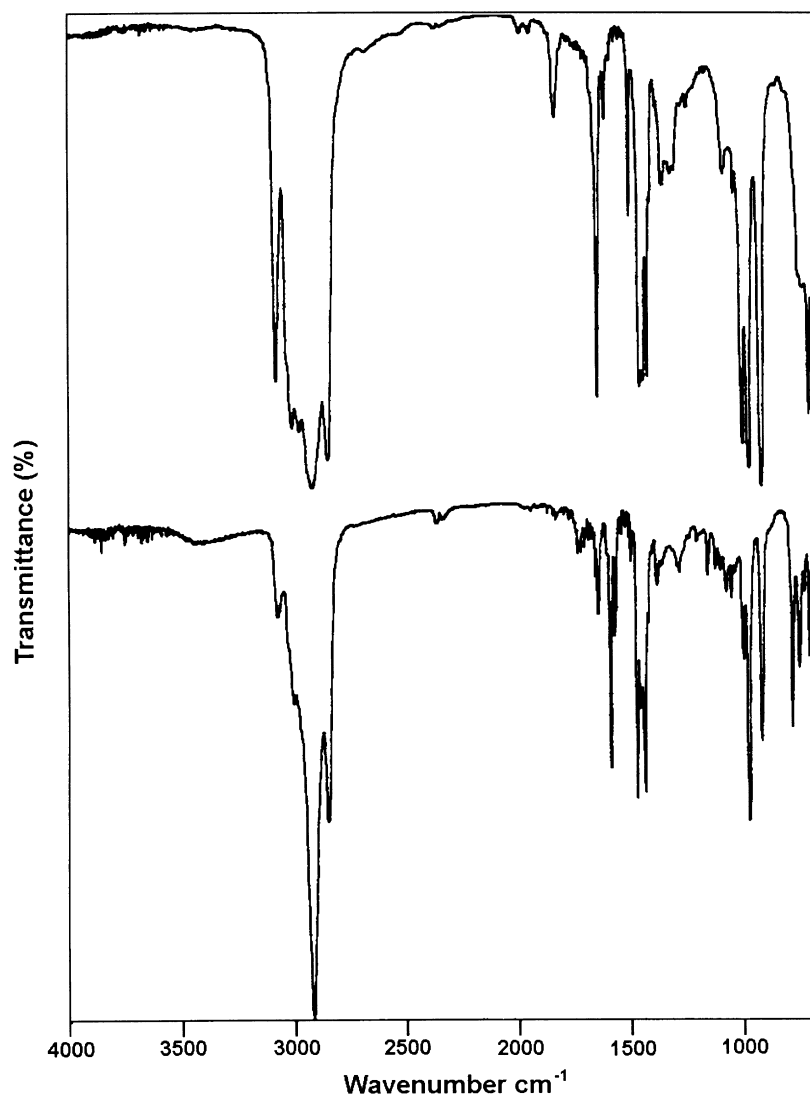


Fig. 3. FTIR spectra of **1** (top) and functionalized polymer **6a** (bottom).

Table 1

Results of the coupling reaction of **1** with IPP

Run	PTPB:IPP:Rh(I)	Reaction time (h)	Product	Conversion ratio (%)	Isolated yield (%)
1	1:1:0.1	24	<b>6a</b>	48	94
2	1:1:0.1	48	<b>6b</b>	50	83
3	1:2:0.1	24	<b>6c</b>	21	94
4	1:0.8:0.08	24	<b>6d</b>	45	93
5	1:0.6:0.06	24	<b>6e</b>	28	95
6	1:0.43:0.043	24	<b>6f</b>	15	98
7	1:0.27:0.027	24	<b>6g</b>	6	99

Table 2

Results of the coupling reaction of PTPBs **2–5** with IPP

Run	PTPB:IPP:Rh(I)	Polymer	Reaction time (h)	Product	Conversion ratio (%)	Isolated yield (%)
1	1:1:0.1	<b>2</b>	24	<b>6h</b>	52	95
2	1:1:0.1	<b>3</b>	24	<b>6i</b>	50	90
3	1:1:0.1	<b>4</b>	24	<b>7a</b>	45	74
4	1:1:0.1	<b>5</b>	24	<b>7b</b>	43	70

#### 4. Conclusion

Rhodium-catalyzed functionalization of vinyl groups in polybutadienes with IPP was achieved successfully. When 1 equiv. of IPP used, PTPBs **1–3**, 99% unsaturated, gave about 50% of conversion ratio in the presence of 10 mol% of RhCl(PPh<sub>3</sub>)<sub>3</sub>. PTPBs **4–5**, 60% unsaturated, gave about 45% of conversion ratio in vinyl groups. As various amounts of substrate used, different conversion ratios in vinyl moiety of PTPBs were obtained.

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