Supporting Information
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Modification of Polybutadiene: Chelation-Assisted Hydroacylation of α,ω-Diol with a Rhodium(I) Catalyst

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Supporting Information

General Information

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography were monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as a visualizing agent p-anisaldehyde solution, and heat as developing agent. NMR spectra were recorded in CDCl$_3$ on a Bruker Advance DPX 250 ($^1$H NMR, 250 MHz; $^{13}$C NMR, 62.9 MHz), and the chemical shift was expressed in ppm relative to TMS. Infrared (IR) spectra were recorded on Nicolet Impact 400 spectrometer.

Typical Procedure for the Catalytic Reaction of 1a and 7a (Table 1, entry 5)

A screw-capped pressure vial (1 mL) equipped with a magnetic stirring bar was charged with 60 mg of polybutadiene (1a, 0.5 mmol), 219 mg of 1,8-octanediol (7a, 1.5 mmol), 23.1 mg of of (PPh$_3$)$_3$RhCl (3, 0.025 mmol), 54 mg of 2-amino-4-picoline (4, 0.5 mmol), 6.1 mg of benzoic acid (5, 0.05 mmol) and 100 mg of 1,4-dioxane. The reaction mixture was sealed and stirred for 12 h in an oil bath that was preheated at 150 °C. After cooling to room temperature, the organic layer was purified by column chromatography (SiO$_2$, n-hexane : ethyl acetate = 5 : 2) to afford 53.2 mg (75 %) of product (8e).

**Compound 6a**: IR (CDCl$_3$): 1715 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 7.29-7.17 (br m, in phenyl group), 5.37 (br s, internal -CH=), 4.96 (br s, terminal -CH=CH$_2$), 2.38-2.35 (br m, 4 H, -CH$_2$ of carbonyl group), 0.93-0.83 (br m, 6 H, CH$_3$ in ethyl group); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta$ = 211.8 (CO), 143.5, 130.6-126.0, 114.4, 42.7-11.2.

**Compound 6b**: IR (CDCl$_3$): 1716 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 7.28-7.15 (br m, in phenyl group), 5.38 (br s, internal -CH=), 4.98 (br s, terminal -CH=CH$_2$), 2.41-2.35 (br m, 4 H, -CH$_2$ of carbonyl group), 0.97-0.83 (br m, 6 H, CH$_3$ in ethyl group); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta$ = 211.5 (CO), 142.9, 130.2-125.8, 114.3, 42.6-11.0.
**Compound 6c:** IR (CDCl$_3$): 1715 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 5.36$ (br s, internal -CH=), 4.94 (br s, terminal -CH=CH$_2$), 2.37 (br s, 4 H, -CH$_2$ of carbonyl group), 0.98-0.82 (br m); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta = 211.5$ (CO), 129.6-128.4, 44.8-10.5.

**Compound 8c:** IR (CDCl$_3$): 1717 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.26$-7.15 (br m, in phenyl group), 5.56-5.38 (br s, internal -CH=), 4.98-4.96 (br s, terminal -CH=CH$_2$), 3.67-3.61 (t, 2 H, -CH$_2$ of alcohol group), 2.43-2.31 (br m, 4 H, -CH$_2$ of carbonyl group), 0.88-0.81 (br s, 3 H, CH$_3$ in ethyl group); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta = 209.6$ (CO), 143.0, 132.3-125.8, 114.5, 62.8 (\(\alpha\)-carbon of alcohol group), 43.6-11.2.

**Compound 8d:** IR (CDCl$_3$): 1716 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.30$-7.16 (br m, in phenyl group), 5.53-5.36 (br s, internal -CH=), 5.01-4.93 (br s, terminal -CH=CH$_2$), 3.65-3.59 (t, 2 H, -CH$_2$ of alcohol group), 2.40-2.33 (br m, 4 H, -CH$_2$ of carbonyl group), 0.85-0.81 (br s, 3 H, CH$_3$ in ethyl group); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta = 210.4$ (CO), 143.7, 130.6-128.6, 114.5, 63.5 (\(\alpha\)-carbon of alcohol group), 44.3-11.3.

**Compound 8e:** IR (CDCl$_3$): 1714 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.33$-7.18 (br m, in phenyl group), 5.55-5.37 (br s, internal -CH=), 5.05-4.96 (br s, terminal -CH=CH$_2$), 3.64-3.59 (t, 2 H, -CH$_2$ of alcohol group), 2.37-2.35 (br m, 4 H, -CH$_2$ of carbonyl group), 0.84-0.81 (br s, 3 H, CH$_3$ in ethyl group); $^{13}$C NMR (77.26 MHz, CDCl$_3$): $\delta = 210.2$ (CO), 143.2, 130.6-128.6, 114.7, 63.3 (\(\alpha\)-carbon of alcohol group), 44.1-11.2.

**Compound 8f:** IR (CDCl$_3$): 1715 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.28$-7.15 (br m, in phenyl group), 5.54-5.35 (br s, internal -CH=), 5.02-4.95 (br s, terminal -CH=CH$_2$), 3.63-3.60 (t, 2 H, -CH$_2$ of alcohol group), 2.36-2.33 (br m, 4 H, -CH$_2$ of carbonyl group), 0.85-0.81 (br s, 3 H, CH$_3$ in ethyl group);
\[ ^{13}\text{C NMR (77.26 MHz, CDCl}_3\text{): } \delta = 211.2 \text{ (CO), 143.6, 130.6-128.6, 114.5, 63.1 (}\alpha\text{-carbon of alcohol group), 44.5-11.5.} \]

**Compound 8g**: IR (CDCl\(_3\)): 1715 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 7.33-7.18 \) (br m, in phenyl group), 5.38 (br s, internal -\( \text{CH=}\)), 4.96 (br s, terminal -\( \text{CH=CH}_2\)), 3.65-3.60 (\( t, 2 \text{ H, -CH}_2\) of alcohol group), 2.37-2.34 (br m, 4 H, -\( \text{CH}_2\) of carbonyl group), 0.88-0.80 (br s, 3 H, CH\(_3\) in ethyl group); \(^{13}\)C NMR (77.26 MHz, CDCl\(_3\)): \( \delta = 210.3 \) (CO), 143.3, 132.4-128.6, 114.5, 63.3 (\( \alpha\)-carbon of alcohol group), 32.9-24.1.

**Compound 9a**: IR (CDCl\(_3\)): 1712 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 7.25-7.17 \) (br m, in phenyl group), 5.38 (br s, internal -\( \text{CH=}\)), 4.95 (br s, terminal -\( \text{CH=CH}_2\)), 2.41-2.37 (br m, 8 H, -\( \text{CH}_2\) of carbonyl group), 0.88 (br s, 17 H, -(CH\(_3\))\(_3\) and -CH\(_3\) in ethyl group); \(^{13}\)C NMR (77.26 MHz, CDCl\(_3\)): \( \delta = 210.2 \) (CO), 143.1, 133.0-128.5, 114.4, 42.9-24.0.

**Compound 9b**: IR (CDCl\(_3\)): 1710 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 7.24-7.18 \) (br m, in phenyl group), 5.38 (br s, internal -\( \text{CH=}\)), 4.95 (br s, terminal -\( \text{CH=CH}_2\)), 2.43-2.35 (br m, 8 H, -\( \text{CH}_2\) of carbonyl group), 0.88 (br s, 3 H, -\( \text{CH}_3\) in ethyl group); \(^{13}\)C NMR (77.26 MHz, CDCl\(_3\)): \( \delta = 211.2 \) (CO), 142.6, 133.8-125.5, 114.2, 42.7-10.9.