



add the vinyl group of **4a** in anti-Markovnikoff's fashion.<sup>11</sup> The conversion rate of the vinyl group to the ketone group can be calculated by the integration ratio of m/(m+n).<sup>12</sup> The reactivity of aldehyde varies with the substituent in a phenyl group of benzaldehyde derivative.

Aldehyde **2a** bearing the dimethylamino group (entry 1) is most reactive and **2g** having the trifluoromethyl group (entry 7) is least reactive. This means that reactivity of the aldehydes is related to the electronic effect of the substituent in the phenyl group. The electron-donating substituent in the phenyl group of benzaldehyde accelerates hydroacylation, while electron-withdrawing substituent retards the rate of hydroacylation (entry 6 & 7). In the case of a moderately electron-donating substituent such as the methoxy and methyl group, about 40% of the vinyl group in **1** was hydroacylated (entry 2 & 3). The thiomethylphenyl group shows no improvement compared with phenyl group bearing no substituent (entry 4 & 5). In the case of ferrocenecarboxaldehyde (**2h**), it was observed that only 21% of the vinyl group was hydroacylated (entry 8) although the ferrocenyl group is regarded as a very electron-rich group. The reason must be that the bulkiness of the ferrocenyl group may play an important role for this hydroacylation. One equimolar addition of PPh<sub>3</sub> is required for a good result. Without adding PPh<sub>3</sub>, the conversion rate of **2a** to **5a** was dropped to 36% from 60%. Added triphenylphosphine is supposed to enhance the catalytic activity of the rhodium complex, probably due to freshly regenerated RhCl(PPh<sub>3</sub>)<sub>3</sub> from *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] which is partly generated from the decarbonylation of aldehyde or from the exchange with oxidized phosphine, PPh<sub>3</sub>=O.<sup>13</sup>

In conclusion, the vinyl group in polybutadiene is directly hydroacylated with aromatic aldehyde.<sup>14</sup> Electron-donating substituent in benzaldehyde showed better conversion rate than electron-withdrawing one.

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- General procedure for the preparation of hydroacylated polybutadiene 5a-5h.** A screw-capped vial was charged with 37 mg (0.04 mmol) of Wilkinson's Complex (**3**) dissolved in 1 mL of toluene and 100 mg of PTPB (**1**) was added. To this mixture 0.4 mmol of aldehyde (**2**), 43.3 mg (0.4 mmol) of 2-amino-3-picoline (**4**), 10.5 mg (0.4 mmol) of triphenylphosphine and 0.28 mmol of H<sub>2</sub>O were added. The resulting solution was heated at 130 for 24 h, and purified by a column-chromatograph (hexane:ethylacetate=2:5) to give the corresponding hydroacylated PTPB **5a-5h**.  
**Spectroscopic Data of 5a:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.87 (d, Hs-2,6 in phenyl ring), 7.64 (d, Hs-3,5 in phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 3.04 (s, (CH<sub>3</sub>)<sub>2</sub>N-), 2.83 (t, -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 199.0 (C=O), 153.3-110.7 (phenyl, -CH= & CH<sub>2</sub>=), 40.0 ((CH<sub>3</sub>)<sub>2</sub>N-), 36.4-27.4 (saturated CH and CH<sub>2</sub>), 35.4 ( $\alpha$ -CH<sub>2</sub> to CO); IR (neat) 3073, 3005, 2918s, 2846, 1667s (C=O), 1446, 1367, 1186, 1065, 820. **5b:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.93 (d, Hs-2,6 in phenyl ring), 6.92 (d, Hs-3,5 in phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 3.85 (s, OCH<sub>3</sub>), 2.88 (m,  $\alpha$ -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 199.3 (C=O), 142.7-113.7 (phenyl, -CH=CH- & CH<sub>2</sub>=), 55.4 (OCH<sub>3</sub>), 36.4-27.4 (saturated

CH and CH<sub>2</sub>), 35.7 ( $\alpha$ -CH<sub>2</sub> to CO); IR (neat) 3074, 3006, 2917s, 2845, 1682s (C=O), 1601, 1258, 834. **5c**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.85 (d, phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 2.91 (t,  $\alpha$ -CH<sub>2</sub> to CO), 2.34 (s, CH<sub>3</sub> in phenyl ring) 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 200.3 (C=O), 143.5-114.2 (phenyl, -CH=CH- & CH<sub>2</sub>=), 35.9 ( $\alpha$ -CH<sub>2</sub> to CO), 21.6 (CH<sub>3</sub> in phenyl ring); IR (neat) 3073, 3006, 2918s, 2846, 1667s (C=O), 1608, 1290, 1180, 817. **5d**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.86 (d, phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 2.89 (m,  $\alpha$ -CH<sub>2</sub> to CO), 2.51 (s, SCH<sub>3</sub>), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 199.6 (C=O), 142.7-114.2 (phenyl, -CH=CH- & CH<sub>2</sub>=), 36.4-27.4 (saturated CH and CH<sub>2</sub>), 35.8 ( $\alpha$ -CH<sub>2</sub> to CO) 14.8(SCH<sub>3</sub>); IR (neat) 3074, 3006, 2918s, 2846, 1682s(C=O), 1590, 1288, 1184, 1093, 815. **5e**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.95-7.47 (m, phenyl ring), 5.7-5.3 (br, -CH=), 4.98 (br, CH<sub>2</sub>=), 2.94 (br,  $\alpha$ -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 200.6 (C=O), 143.0-114.2 (phenyl, -CH=CH- & CH<sub>2</sub>=), 36.4-27.4 (saturated CH and CH<sub>2</sub>), 36.0 ( $\alpha$ -CH<sub>2</sub> to CO) ; IR (neat) 3073, 3006, 2917s, 2846, 1688s, 1597, 1026, 1179, 542. **5f**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.99-7.94 (m, Hs-2,3,5,6 in phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br,

CH<sub>2</sub>=), 2.91 (br,  $\alpha$ -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) (ppm) 198.9 (C=O), 167.3 (C-4 in phenyl ring), 142.7-114.2 (phenyl, -CH=CH- & CH<sub>2</sub>=), 36.4-27.4 (saturated CH and CH<sub>2</sub>), 36.0 ( $\alpha$ -CH<sub>2</sub> to CO) ; IR (neat) 3074, 3007, 2917s, 2846, 1688s, 1598, 1233, 1119, 840. **5g**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.04 (d, Hs-2,6 in phenyl ring), 7.72 (d, Hs-3,5 in phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 2.96 (br,  $\alpha$ -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 199.4(C=O), 143.1-114.2 (phenyl, -CH=CH- & CH<sub>2</sub>=), 124.5 (CF<sub>3</sub>), 36.4-27.4 (saturated CH and CH<sub>2</sub>), 36.3 ( $\alpha$ -CH<sub>2</sub> to CO); IR (neat) 3074, 3007, 2917s, 2846, 1696s (C=O), 1639, 1324, 1171, 1134, 849. **5h**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 5.7-5.3 (br, -CH=), 4.96 (br, CH<sub>2</sub>=), 4.77 (br, Hs-2,5 in substituted Cp), 4.48 (br, Hs-3,4 in substituted Cp), 4.19 (s, unsubstituted Cp), 2.66 (br,  $\alpha$ -CH<sub>2</sub> to CO), 2.2-1.1 (m, saturated CH<sub>2</sub> and CH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 204.6 (C=O), 145.6-125.2 (=CH-), 114.3 (CH<sub>2</sub>=), 72.1 (C-2,5 in substituted Cp), 69.7 (C-3,4 unsubstituted Cp), 37.1 ( $\alpha$ -CH<sub>2</sub> to CO), 36.3-27.4 (saturated CH and CH<sub>2</sub>) ; IR (neat) 3100, 3000, 2920s, 2840, 1670s, 1450, 1380, 1250, 1110, 1050, 970, 820.