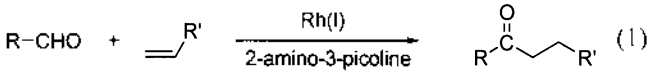
Direct Hydroacylation of Polybutadiene by Wilkinson's Complex

Jae-Hun Kim† and Chul-Ho Jun*

†*Division of Organic Synthesis, Kukje Pharmaceutical R&D Center, Seoul 143-210, Korea*
Department of Chemistry, Yonsei University, Seoul 120-749, Korea
Received September 15, 1998

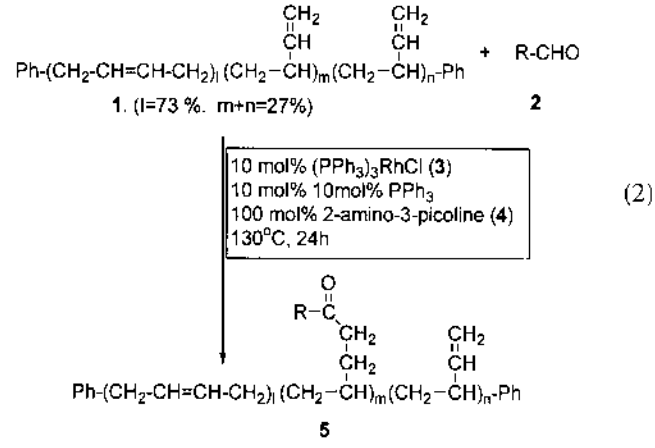
It has always been a goal of polymer scientists to prepare well-established functional polymers with desirable physical properties and functional groups.[1] Polybutadiene is a good starting material for this purpose, since the desirable functional group could be introduced into an available unsaturated site in this polymer. A variety of methods for chemical modification of polybutadiene for a new specialty polymer have been reported: hydroformylation,[2] aminomethylation[3], hydrocarboxylation,[4] hydrosilation,[5] and hydrogenation.[6] Chemical modification of polybutadiene *via* catalytic hydroacylation offers an efficient synthetic route to novel polymers containing ketone functional groups. Catalytic introduction of the acyl group into polybutadiene has already been reported:[7] hydroiminoacylation of polybutadiene with carboxaldimine, followed by hydrolysis of the resulting ketimine-impregnated polybutadiene.



(1)

This indirect modification of polybutadiene requires several steps to achieve C-C bond coupling. Recently we developed a direct chelation-assisted hydroacylation method of 1-alkene with aldehyde using 2-amino-3-picoline (eq. 1),[8] and it has been further extended to the hydroacylation of primary alcohol.[9] Here, we report a method for incorporating the acyl groups into non-functionalized polybutadiene.

Polybutadiene (**1**: phenyl-terminated polybutadiene consisted of 27% of the vinylic olefin and 73% of the internal olefin; average M.W. 3400) was allowed to react with 4-dimethylaminobenzaldehyde (**2a**) at 130 °C for 24 h under the mixture of 10 mol% of $RhCl(PPh_3)_3$ (**3**), 10 mol% of PPh_3, 0.28 mmol of H_2O and 100 mol% of 2-amino-3-picoline (**4**).



(2)

After the reaction, the resulting mixture was purified by column chromatography to give the 4-*N,N*-dimethylaminobenzoyl group-impregnated polymer **5a** in a 60% conversion rate (60% of the vinyl group in **1** is converted into a 4-*N,N*-dimethylaminobenzoylethyl group). Polymer **4** was characterized by IR, ^1H NMR and ^{13}C NMR spectra. The IR band of the carbonyl group appears at 1667 cm^{-1}. The intensity of the vinyl group (-CH=CH_2) at 911 cm^{-1} diminishes while that of the trans-1,4-internal olefin at 967 cm^{-1} and the cis-1,4-internal olefin at 699 cm^{-1} still remain unchanged.[10] The ^{13}C NMR spectra also show the characteristic peaks of **5a**. The newly formed α-CH_2 group next to the carbonyl group appears at 35.4 ppm, and the carbonyl group appears at 199.0 ppm. In the ^1H NMR spectrum, α-CH_2 group next to the carbonyl group in linear alkyl ketone appears at 2.8 ppm. No signal around 3.5 ppm from the secondary CH group attached to the carbonyl group was found, implying that any branched alkyl ketone was not formed. This explains partly that the real active species is aldimine, generated from aldehyde and 2-amino-3-picoline, since sterically hindered iminoacylrhodium(III)hydride intermediate should

Table 1. Hydroacylation of Polybutadiene (**1**) with Various Aldehydes (**2**)

Entry	R-	Aldehyde(2)	Hydroacylated Product (5)	Conversion rate (m/m+n)
1	Me_2N–	(2a)	(5a)	60%
2	CH_3O–	(2b)	(5b)	42%
3	CH_3–	(2c)	(5c)	41%
4	CH_3S–	(2d)	(5d)	30%
5		(2e)	(5e)	32%
6	F–	(2f)	(5f)	23%
7	CF_3–	(2g)	(5g)	8%
8	Fe	(2h)		21%

add the vinyl group of **4a** in anti-Markovnikoff's fashion.[11] The conversion rate of the vinyl group to the ketone group can be calculated by the integration ratio of m/(m+n).[12] 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_3 is required for a good result. Without adding PPh_3, the conversion rate of **2a** to **5a** was dropped to 36% from 60%. Added triphenylphospine is supposed to enhance the catalytic activity of the rhodium complex, probably due to freshly regenerated $RhCl(PPh_3)_3$ from *trans*-$[RhCl(CO)(PPh_3)_2]$ which is partly generated from the decarbonylation of aldehyde or from the exchange with oxidized phosphine, PPh_3=O.[13]

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

Acknowledgement. This research was supported by the Korea Science and Engineering Foundation (Grant No. 97-05-01-05-01-3) and the Ministry of Education (Project No. BSRI-97-3422). Authors thank Mr. Jae-Bum Park for technical assistance.

References

1. (a) Kokufuta, E. *Adv. Polym. Sci.* **1993**, *110*, 157. (b) Ohata, M.; Yamamoto, M.; Tacano, A.; Isono, Y. *J. Appl. Polym. Sci.* **1996**, *59*, 399. (c) Belfield, K. D.; Wang, A. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 1235. (d) Frechet, J. M. J.; Darling, G. D.; Itsuno, S.; Lu, P.-Z.; de Meftahi, M. V.; Rolls, Jr.; W. A. *Pure. Appl. Chem.* **1988**, *60*, 353. (e) Soutif, J.-C.; Brosse, J.-C. *Reactive Polymers* **1990**, *12*, 3.
2. (a) Mohammadi, N. A.; Ling, S. S.; Rempel, G. L. *Polym. Prepr.* **1986**, *27*, 95. (b) Tremont, S. J.; Remsen, E. E.; Mills, P. L. *Macromolecules* **1990**, *23*, 1984. (c) Mills, P. L.; Tremont, S. J.; Remsen, E. E. *Ind. Eng. Chem. Res.* **1990**, *29*, 1443. (d) Scott, P. J.; Rempel, G. L. *Macromolecules* **1992**, *25*, 2811.
3. (a) McEntire, E. E.; Knifton, J. F.; U. S. Patent 4,657,984 **1987**; *Chem. Abstr.* **1987**, 116163n. (b) Wideman, L. G.; U. S. Patent 5,134,200, **1992**; *Chem. Abstr.* **1992**, 28574y.
4. (a) Narayanan, P.; Clubley, B. G.; Cole-Hamiltone, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1628. (b) Narayanan, P.; Kaye, B.; Cole-Hamiltone, D. J. *J. Mater. Chem.* **1993**, *3*, 119.
5. (a) Guo, X.; Farwaha, R.; Rempel, G. L. *Macromolecules* **1990**, *23*, 5047. (b) Guo, X.; Rempel, G. L. *Macromolecules* **1992**, *25*, 883. (c) Iraqi, A.; Seth, S.; Vincent, V. A.; Cole-Hamiltone, D. J.; Watkinson, M. D.; Graham, I. M.; Jeffery, D. *J. Mater. Chem.* **1992**, *2*, 1057.
6. (a) Rosedale, J. H.; Bates, F. S. *J. Am. Chem. Soc.* **1988**, *110*, 3542. (b) Gehlson, M. D.; Bates, F. S. *Macromolecules* **1993**, *26*, 4122. (c) Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *Ind. Eng. Chem. Res.* **1991**, *30*, 1086. (d) Bhattacharjee, S.; Bhowmick, A. K.; Avasthi, B. N. *J. Appl. Polym.Sci.* **1990**, *41*, 1357. (e) Gilliom, L. R. *Macromolecules* **1989**, *22*, 662.
7. Jun, C. -H.; Kang, J.-B.; Kim, J.-Y. *J. Organomet. Chem.* **1993**, *458*, 193.
8. Jun, C.-H.; Lee, H.; Hong, J.-B. *J. Org. Chem.* **1997**, *62*, 1200.
9. (a) Jun, C.-H.; Huh, C.-W.; Na, S.-J. *Angew. Chem., Int. Ed.* **1998**, *37*, 145. (b) Jun, C.-H.; Hwang, D.-C. *Polymer* **1998**, *39*, 7143.
10. Haslam, J.; Willis, H. A.; Squirrell, D. C. M. In *Identification and Analysis of Plastics*; Heyden: London, **1972**; p 441.
11. For detailed mechanism of hydroiminoacylation: Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640.
12. Letter m is the hydroacylated α-CH_2 to CO assigned at 2.8 ppm, and n is the unreacted terminal vinylic CH_2 group assigned at 4.9 ppm.
13. Geoffroy, G. L.; Denton, D. A.; Kenney, M. E.; Bucks, R. R. *Inorg. Chem.* **1976**, *15*, 2382.
14. **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 triphenylphospine and 0.28 mmol of H_2O 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: ^{1}H NMR (300 MHz, $CDCl_3$) δ (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_2=), 3.04 (s, $(CH_3)_2N$-), 2.83 (t, -CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.0 (C=O), 153.3-110.7 (phenyl, -CH= & CH_2=), 40.0 ($(CH_3)_2N$-), 36.4-27.4 (saturated CH and CH_2), 35.4 (α-CH_2 to CO); IR (neat) 3073, 3005, 2918s, 2846, 1667s (C=O), 1446, 1367, 1186, 1065, 820. **5b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (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_2=), 3.85 (s, OCH_3), 2.88 (m, α-CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.3 (C=O), 142.7-113.7 (phenyl, -CH=CH- & CH_2=), 55.4 (OCH_3), 36.4-27.4 (saturated

CH and CH_2), 35.7 (α-CH_2 to CO); IR (neat) 3074, 3006, 2917s, 2845, 1682s (C=O), 1601, 1258, 834. **5c**: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm) 7.85 (d, phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH_2=), 2.91 (t, α-CH_2 to CO), 2.34 (s, CH_3 in phenyl ring) 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.3 (C=O), 143.5-114.2 (phenyl, -CH=CH- & CH_2=), 35.9 (α-CH_2 to CO), 21.6 (CH_3 in phenyl ring); IR (neat) 3073, 3006, 2918s, 2846, 1667s (C=O), 1608, 1290, 1180, 817. **5d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86 (d, phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH_2=), 2.89 (m, α-CH_2 to CO), 2.51 (s, SCH_3), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.6 (C=O), 142.7-114.2 (phenyl, -CH=CH- & CH_2=), 36.4-27.4 (saturated CH and CH_2), 35.8 (α-CH_2 to CO) 14.8(SCH_3); IR (neat) 3074, 3006, 2918s, 2846, 1682s(C=O), 1590, 1288, 1184, 1093, 815. **5e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95-7.47 (m, phenyl ring), 5.7-5.3 (br, -CH=), 4.98 (br, CH_2=), 2.94 (br, α-CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 200.6 (C=O), 143.0-114.2 (phenyl, -CH=CH- & CH_2=), 36.4-27.4 (saturated CH and CH_2), 36.0 (α-CH_2 to CO) ; IR (neat) 3073, 3006, 2917s, 2846, 1688s, 1597, 1026, 1179, 542. **5f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.99-7.94 (m, Hs-2,3,5,6 in phenyl ring), 5.7-5.3 (br, -CH=), 4.96 (br, CH_2=), 2.91 (br, α-CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) (ppm) 198.9 (C=O), 167.3 (C-4 in phenyl ring), 142.7-114.2 (phenyl, -CH=CH- & CH_2=), 36.4-27.4 (saturated CH and CH_2), 36.0 (α-CH_2 to CO) ; IR (neat) 3074, 3007, 2917s, 2846, 1688s, 1598, 1233, 1119, 840. **5g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (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_2=), 2.96 (br, α-CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 199.4(C=O), 143.1-114.2 (phenyl, -CH=CH- & CH_2=), 124.5 (CF_3), 36.4-27.4 (saturated CH and CH_2), 36.3 (α-CH_2 to CO); IR (neat) 3074, 3007, 2917s, 2846, 1696s (C=O), 1639, 1324, 1171, 1134, 849. **5h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.7-5.3 (br, -CH=), 4.96 (br, CH_2=), 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, α-CH_2 to CO), 2.2-1.1 (m, saturated CH_2 and CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 204.6 (C=O), 145.6-125.2 (=CH-), 114.3 (CH_2=), 72.1 (C-2,5 in substituted Cp), 69.7 (C-3,4 unsubstituted Cp), 37.1 (α-CH_2 to CO), 36.3-27.4 (saturated CH and CH_2) ; IR (neat) 3100, 3000, 2920s, 2840, 1670s, 1450, 1380, 1250, 1110, 1050, 970, 820.