Electronic Supplementary Information

A Catalytic Hydroesterification Process Using HCO$_2$Na, Ru$_3$(CO)$_{12}$ and Alcohols for Preparing Ester Modified Polybutadienes

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1. General

$^1$H NMR and $^{13}$C NMR were recorded on a Bruker Advance II/DPX 400(400 MHz $^1$H, 100 MHz $^{13}$C) spectrometers and chemical shifts are reported relative to residual deuterated solvent peaks. $^1$H NMR spectra were referenced to CD$_2$Cl$_2$ (for $^1$H, $\delta = 5.32$ ppm) as an internal standard and are reported as chemical shift multiplicity: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. $^{13}$C NMR spectra were referenced to the residual CDCl$_3$ (for $^{13}$C, $\delta = 77.26$ ppm) as internal standard. Infrared spectra were obtained on a Bruker Vertex70 spectrometer. Fluorescence spectra were obtained on a Perkin Elmer LS 55. Thermo Gravimetric Analysis (TGA) was carried out using a Perkin Elmer STA8000, with heating from 30 to 600 °C at a heating rate of 20 °C/min. Differential Scanning Calorimetry (DSC) was carried out using a Perkin Elmer DSC 8000, with heating from -80 to 100 °C, in N$_2$ atmosphere, at a flow rate of 20 mL/min. Analytical GPC was performed on a JASCO HPLC equipped with HF-404HQ columns (ID. 4.6 X L. 250 mm, Shodex, Tokyo, Japan) using THF as the eluent at a flow rate of 1.0 ml/min.

2. Materials

Polybutadiene (1) which contains 45% vinyl, 5% cis-1,4 internal olefin, 10% trans-1,4 internal olefin and 40% saturated part was purchased from Aldrich and its average molecular weight is 1800. Most reagent grade chemicals [1,4-dioxane, acetonitrile, dichloromethane, 1, 2a-c, 3a, 3b, 3d-g, 3i-k, 4a, 5a, pyrene, ferrocene carboxaldehyde, cyclobutane carboxylic acid, copper(II) perchlorate hexahydrate, zinc(II) perchlorate hexahydrate, calcium(II) perchlorate tetrahydrate, cadmium(II) perchlorate hydrate, magnesium(II) perchlorate, nickel(II) perchlorate hexahydrate and cobalt(II) perchlorate hexahydrate] were purchased from Aldrich, Acros Organics and TCI Chemical Company and used as received unless otherwise stated. Cyclobutylmethanol (3c) was prepared by reduction of cyclobutanecarboxylic acid using lithium aluminum hydride. Ferrocenyilmethanol (3h) was prepared by reduction of ferrocene carboxaldehyde using lithium aluminum hydride. Pyrenylmethyl alcohol (3l) was prepared by Rieche formylation of pyrene followed by reduction of the resulting aldehyde using lithium aluminum hydride.

3. Experimental

- A typical procedure for synthesis of modified polybutadiene (Table 1, entry 1)
A 5 mL pressure vial was charged with polybutadiene (1, 50 mg, (0.416 mmol of vinyl group)), sodium formate (2a, 56.6 mg, (0.832 mmol)), 2-phenylethyl alcohol (3a, 61.0 mg, (0.499 mmol)), Ru₃(CO)₁₂ (4a, 13.4 mg, (0.02095 mmol)), 2-pyridinemethanol (5a, 9.1 mg, (0.0832 mmol)) and 1,4-dioxane (1 mL). The mixture was stirred at 150 °C for 6 h. After cooling to room temperature, the mixture was concentrated in vacuo, and the residue was washed thoroughly with methanol and dried to give the 2-phenylethyl ester containing modified polybutadiene (6a).

- A typical procedure for synthesis of modified polybutadiene with 1:1 ratio of mixed esters (Table 3, entry 1)

A 5 mL pressure vial was charged with polybutadiene (1, 50 mg, (0.416 mmol of vinyl group)), sodium formate (2a, 56.6 mg (0.832 mmol)), 2-phenylethyl alcohol (3a, 50.8 mg (0.416 mmol)), heptanol (3b, 48.3 mg (0.416 mmol)), Ru₃(CO)₁₂ (4a, 13.4 mg, (0.02095 mmol)), 2-pyridinemethanol (5a, 9.1 mg, (0.0832 mmol)) and 1,4-dioxane (1 mL). The mixture was stirred at 150 °C for 6 h. After cooling to room temperature, the mixture was concentrated in vacuo, and the residue was washed thoroughly with methanol and dried to give the 1:1 ratio of 2-phenylethyl and heptyl ester containing modified polybutadiene (7a).

- Measurements of fluorescence spectra of 7l in the presence of various metal(II) cations

The fluorescence spectra were recorded following addition of various concentrations (0-40 x 10⁻⁶ M) of copper(II) perchlorate hexahydrate in acetonitrile (1 mL) into polybutadiene modified with pyrenylmethyl ester (7l) in 1 mL of dichloromethane (Figure 2a). Solutions of 7l (5 x 10⁻⁶ M, based on pyrenylmethyl ester group in modified polybutadiene) in 1 mL of dichloromethane were independently treated with 40 x 10⁻⁶ M of metal(II) perchlorates (Zn²⁺, Ca²⁺, Cd²⁺, Mg²⁺, Ni²⁺, Co²⁺ and Cu²⁺) in 1 mL of acetonitrile. Fluorescence spectra of the mixtures were then recorded.

Polybutadiene (1): 45% of vinyl and 55% of internal olefins and saturated hydrocarbons based on terminal phenyl; ¹H NMR (400 MHz, CD₂Cl₂) δ 7.26-7.24 (br m), 7.18 (br m), 5.86-5.77 (br m), 5.60-5.58 (br m), 5.39-5.31 (br m), 4.97 (br m), 2.66-2.64 (br m), 2.53 (br m), 2.38 (br s), 2.04 (br m), 1.54 (br m), 1.45 (br m), 1.43 (br m), 1.29 (br m), 0.91 (br m), 0.68 (br m), 0.66 (br m); ¹³C NMR (100 MHz, CDCl₃) δ 144.7, 144.4, 143.8, 143.4, 143.2, 142.9, 131.9, 130.8, 130.3, 130.2, 129.8, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 125.9, 125.8, 114.5, 114.4, 114.1, 113.1, 112.2, 111.9, 45.5, 44.0, 43.8, 12.6, 41.8, 41.3, 41.0, 40.5, 39.8, 39.5, 39.3, 39.1, 38.9, 38.4, 37.7, 36.2, 36.1, 35.8, 34.5, 34.4, 34.2, 33.7, 33.0, 32.5, 32.2, 31.6, 30.6, 30.4, 27.8, 27.6, 25.8, 25.2; IR spectrum (CDCl₃) 3076, 2999, 2974, 2918, 2854,
1825, 1639, 1496, 1453, 1417, 1379, 1348, 1294, 1265, 1077, 995, 968, 909, 741, 698, 679 cm⁻¹; \( T_d = 454 \, ^\circ C; \, T_g = -30.2 \, ^\circ C; \, M_n = 2702, \, M_w = 5843, \, \text{PDI} = 2.16. 

2-Phenylethyl ester-containing modified polybutadiene (6a): 28% of 2-phenylethyl ester and the rest (72%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (72% yield, 73.9 mg); \(^1\)H NMR (400 MHz, CD₂Cl₂) \( \delta \) 7.28-7.24 (br m), 5.18-5.10 (br m, internal -CH=CH-), 4.26 (br s), 2.93 (br s), 2.58 (br s), 2.26 (br s), 1.99 (br s), 1.68 (br s), 1.58 (br s), 1.28 (br m), 0.98 (br s), 0.85 (br s); \(^13\)C NMR (100 MHz, CDCl₃) \( \delta \) 174.2 (CO), 138.0, 130.5, 129.8, 129.0, 128.6, 127.7, 126.7, 64.9, 37.1, 36.7, 35.3, 33.1, 32.8, 32.4, 32.0, 29.89, 28.4, 27.8, 27.4, 13.7, 13.4, 12.9, 11.9; IR spectrum (CDCl₃) 2926, 2855, 2097, 1977, 1945, 1735, 1670, 1497, 1455, 1378, 1260, 1164, 747, 699 cm⁻¹; \( T_d = 306 \, ^\circ C, 415 \, ^\circ C; \, T_g = -11.2 \, ^\circ C; \, M_n = 4716, \, M_w = 10868, \, \text{PDI} = 2.30. 

Heptyl ester-containing modified polybutadiene (6d): 23% of heptyl ester and the rest (77%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (88% yield, 90.1 mg); \(^1\)H NMR (400 MHz, CD₂Cl₂) \( \delta \) 7.25 (br s), 7.16 (br s), 5.38-5.09 (br m, internal -CH=CH-), 4.02 (br s), 2.57 (br s), 2.27 (br s), 1.98 (br s), 1.58 (br s), 1.28 (br m), 0.96 (br s), 0.89 (br s); \(^13\)C NMR (100 MHz, CDCl₃) \( \delta \) 174.4 (CO), 128.5, 64.6, 32.8, 32.6, 31.9, 29.9, 29.1, 28.8, 28.4, 26.1, 22.8, 14.3, 13.5, 13.1, 12.9; IR spectrum (CDCl₃) 2959, 2926, 2856, 2047, 1978, 1947, 1737, 1456, 1378, 1254, 1167, 1066, 968, 874, 758, 699 cm⁻¹; \( T_d = 254 \, ^\circ C, 396 \, ^\circ C; \, T_g = -23.4 \, ^\circ C; \, M_n = 4778, \, M_w = 11869, \, \text{PDI} = 2.48. 

Methylcyclobutyl ester-containing modified polybutadiene (6e): 21% of methylcyclobutyl ester and the rest (79%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (84% yield, 82.0 mg); \(^1\)H NMR (400 MHz, CD₂Cl₂) \( \delta \) 7.25 (br s), 7.17 (br s), 5.32-5.10 (br m, internal -CH=CH-), 4.01 (br s), 2.60 (br s), 2.29 (br s), 1.99 (br m), 1.77 (br m), 1.57 (br s), 1.27 (br m), 0.96 (br s), 0.85 (br s); \(^13\)C NMR (100 MHz, CDCl₃) \( \delta \) 174.4 (CO), 13.05, 128.4, 125.7, 68.3, 38.9, 37.2, 35.4, 34.3, 33.2, 32.8, 32.1, 31.7, 30.4, 29.9, 28.4, 27.8, 26.9, 26.0, 24.9, 23.2, 18.6, 14.3; IR spectrum (CDCl₃) 2926, 2856, 2061, 2028, 1990, 1946, 1737, 1670, 1457, 1378, 1290, 1251, 1217, 1168, 1100, 969, 910, 807, 758, 699, 667 cm⁻¹; \( T_d = 257 \, ^\circ C, 406 \, ^\circ C; \, T_g = -16.5 \, ^\circ C; \, M_n = 4062, \, M_w = 8184, \, \text{PDI} = 2.01. 

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Benzyl ester-containing modified polybutadiene (6f): 26% of benzyl ester and the rest (74%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (86% yield, 84.9 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.36 (br s), 7.19 (br m), 5.41-5.11 (br m, internal -CH=CH-), 2.60 (br s), 2.36 (br s), 2.01 (br s), 1.59 (br s), 1.30 (br s), 0.99 (br m) 0.87 (br s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.8 (CO), 136.2, 128.6, 128.3, 66.2, 38.2, 37.1, 36.7, 35.9, 33.2, 32.8, 32.4, 30.3, 29.8, 28.7, 28.3, 27.7, 27.4, 13.4, 13.1, 12.9; IR spectrum (CDCl$_3$) 3032, 2959, 2925, 2855, 2047, 1976, 1738, 1493, 1453, 1379, 1258, 1156, 968, 882, 750, 697 cm$^{-1}$; T$_d$ = 308 ºC, 405 ºC; T$_g$ = -13.1 ºC; M$_n$ = 4447, M$_w$ = 10372, PDI = 2.33.

2-Pyridylmethyl ester-containing modified polybutadiene (6g): 23% of 2-pyridylmethyl ester and the rest (77%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (80% yield, 80.1 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.55 (br s), 7.70 (br s), 7.34 (br s), 7.22 (br s), 5.32-5.19 (br m, internal -CH=CH-), 2.60 (br m), 2.42 (br m), 1.99 (br m), 1.58 (br s), 1.28 (br m), 0.97 (br s), 0.86 (br s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.6 (CO), 156.1, 149.5, 141.0, 136.7, 130.4, 128.4, 125.9, 125.6, 123.6, 122.8, 121.8, 66.7, 38.8, 38.3, 37.1, 36.7, 36.1, 32.3, 32.7, 32.3, 31.9, 30.2, 29.8, 29.6, 28.6, 28.3, 27.8, 26.8, 25.9, 13.6; IR spectrum (CDCl$_3$) 2925, 2855, 2046, 2026, 1974, 1943, 1740, 1666, 1633, 1594, 1573, 1454, 1378, 1265, 1240 1156, 1048, 969, 881, 755, 700 cm$^{-1}$; T$_d$ = 296 ºC, 415 ºC; T$_g$ = -10.0 ºC; M$_n$ = 5059, M$_w$ = 11142, PDI = 2.20.

2-Thiopheneethyl ester-containing modified polybutadiene (6h): 16% of 2-thiopheneethyl ester, 8% of vinyl and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (73% yield, 78.6 mg); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.25 (br s), 7.16 (br s), 6.94 (br s), 6.87 (br s), 5.39-5.20 (br m, internal -CH=CH-), 4.95 (br m, vinyl -CH=CH$_2$), 4.26 (br s), 3.14 (br s), 2.70 (br m), 2.63 (br s), 2.30 (br m), 1.98 (br s), 1.56 (br s), 1.27 (br m), 0.95 (br s), 0.85 (br s); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.8 (CO), 140.0, 128.4, 126.9, 125.5, 124.0, 64.5, 44.6, 41.0, 38.9, 37.1, 36.7, 32.7, 32.3, 31.9, 30.7, 29.8, 29.4, 28.6, 28.3, 27.8, 26.8, 25.9, 23.1, 14.3; IR spectrum (CDCl$_3$) 2925, 2855, 2073, 2047, 1997, 1975, 1921, 1738, 1454, 1379, 1244, 1217, 1164, 1079, 1039, 969, 851, 823, 759, 695, 560, 504 cm$^{-1}$; T$_d$ = 391 ºC; T$_g$ = 18.0 ºC; M$_n$ = 4254, M$_w$ = 8926, PDI = 2.10.
4-Pyridylpropyl ester-containing modified polybutadiene (6i): 12% of 4-pyridylpropyl ester, 12% of vinyl and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (71% yield, 80.4 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 8.45 (br s), 7.23 (br s), 7.17 (br s), 7.12 (br s), 5.39-5.18 (br m, internal -CH=CH-), 4.95 (br m, vinyl -CH=CH\(_2\)) 4.06 (br s), 2.68 (br s), 2.30 (br s), 1.97 (br s), 1.78 (br s), 1.56 (br s), 0.85 (br s); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.2 (CO), 150.3, 140.9, 130.5, 129.9, 128.5, 124.0, 63.4, 32.8, 31.7, 29.8, 29.3, 28.3, 27.8, 27.4, 26.8, 13.4, 12.8, 12.0, 11.7; IR spectrum (CDCl\(_3\)) 2921, 2855, 2041, 2022, 1999, 1971, 1938, 1732, 1604, 1573, 1462, 1378, 1218, 1167, 1069, 1028, 995, 969, 880, 838, 798, 769, 700, 666 cm\(^{-1}\); \(T_d\) = 318 °C, 415 °C; The polymer showed no obvious glass transition between -80 and 100 °C; \(M_n = 4071\), \(M_w = 7526\), PDI = 1.85.

4-(2-Hydroxyethyl)phenethyl ester-containing modified polybutadiene (6j): 27% of 4-(2-hydroxyethyl)phenethyl ester and the rest (73%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (70% yield, 77.9 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.16 (br m), 5.32-5.10 (br m, internal -CH=CH-), 4.23 (br s), 3.79 (br s), 2.89-2.81 (br m), 2.59 (br s), 2.27 (br s), 1.99 (br s), 1.57 (br s), 1.27 (br s), 0.97 (br s), 0.85 (br m); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.1 (CO), 136.9, 135.9, 129.2, 129.1, 128.4, 64.9, 63.6, 38.9, 34.8, 32.7, 32.4, 32.0, 29.8, 28.6, 28.3, 13.4, 13.1, 12.8, 12.0, 11.6; IR spectrum (CDCl\(_3\)) 2925, 2855, 2047, 2020, 1997, 1973, 1934, 1736, 1604, 1515, 1456, 1377, 1264, 1162, 1114, 1048, 1022, 968, 811, 761, 738, 699 cm\(^{-1}\); \(T_d\) = 304 °C, 412 °C; \(T_g = 4.3 \, ^\circ C\); \(M_n = 4881\), \(M_w = 12821\), PDI = 2.63.

Ferrocenylmethyl ester-containing modified polybutadiene (6k): 19% of ferrocenylmethyl ester and the rest (81%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (83% yield, 97.2 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.29 (br m) 7.21 (br m), 5.32-5.13 (br m, internal -CH=CH-), 4.92 (br s), 4.29 (br s), 4.19 (br m), 2.65 (br s), 2.31 (br s), 2.00 (br s), 1.60 (br s), 1.29 (br m), 0.99 (br s), 0.87 (br s); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.9 (CO), 139.9, 138.8, 131.7, 130.4, 128.4, 81.4, 69.6, 68.8, 68.6, 62.7, 39.0, 37.0, 32.7, 29.7, 28.2, 13.3, 12.8, 12.0; IR spectrum (CDCl\(_3\)) 2960, 2925, 2855, 2047, 2024, 1973, 1941, 1737, 1603, 1567, 1455, 1377, 1288, 1217, 1155, 1107, 1041, 1001, 968, 874, 818, 758, 698, 637 cm\(^{-1}\); \(T_d = 223 \, ^\circ C, 409 \, ^\circ C\); The polymer showed no obvious glass transition between -80 and 100 °C; \(M_n = 4453\), \(M_w = 9396\), PDI = 2.11.
4-Amino-2-phenylethyl ester-containing modified polybutadiene (6l): 11% of 4-ano2-phenylethyl ester and the rest (89%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (64% yield, 74.6 mg); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.26 (br s), 7.17 (br s), 6.98 (br s), 6.60 (br s), 5.39-5.10 (br m, internal -CH=CH-), 4.17 (br s), 3.64 (br s), 2.79 (br s), 2.60 (br m), 2.27 (br m), 1.98 (br m), 1.74 (br s), 1.67 (br s), 1.57 (br s), 1.27 (br s), 0.97-0.84 (br m); ¹³C NMR (100 MHz, CDCl₃) δ 174.2 (CO), 145.1, 129.9, 128.5, 127.7, 120.3, 115.4, 65.3, 38.8, 37.2, 34.4, 32.8, 32.1, 29.8, 28.4, 13.5, 12.9, 12.0; IR spectrum (CDCl₃) 3464, 3375, 3286, 2925, 2856, 2023, 2002, 1974, 1937, 1733, 1625, 1518, 1455, 1379, 1265, 1165, 1049, 968, 909, 822, 767, 700 cm⁻¹; T_d = 308 °C, 418 °C; T_g = 18.0 °C; Mₙ = 4056, M_w = 8470, PDI = 2.09.

2-Phenylethyl ester and heptyl ester-containing modified polybutadiene (7a): 11% of 2-phenylethyl ester, 11% of heptyl ester and the rest (78%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (83% yield, 82.9 mg); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.27 – 7.23 (br m), 5.32-5.09 (br m, internal -CH=CH-), 4.25 (br s), 4.02 (br s), 2.92 (br s), 2.57 (br s), 2.26 (br s), 1.98 (br s), 1.58 (br s), 1.27 (br s), 0.97 (br s), 0.89-0.84 (br m); ¹³C NMR (100 MHz, CDCl₃) δ 174.1 (CO), 137.9, 129.0, 128.6, 126.6, 64.8, 64.5, 38.7, 36.7, 35.3, 33.3, 32.8, 31.9, 30.7, 30.3, 29.9, 29.1, 28.8, 28.3, 27.8, 26.9, 26.0, 22.7, 14.2; IR spectrum (CDCl₃) 3027, 2959, 2926, 2855, 2073, 2047, 1997, 1977, 1922, 1737, 1662, 1605, 1455, 1378, 1250, 1166, 1049, 1032, 969, 881, 758, 699, 667, 644, 560 cm⁻¹; Mₙ = 4736, M_w = 10811, PDI = 2.28.

2-Phenylethyl ester and 2-thiopheneethyl ester containing modified polybutadiene (7b): 13% of 2-phenylethyl ester, 13% of 2-thiopheneethyl ester and the rest (74%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (54% yield, 55.2 mg); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.27-7.16 (br m), 6.93 (br s), 6.86 (br s), 5.38-5.10 (br m, internal -CH=CH-), 4.25 (br s), 3.13 (br s), 2.91 (br s), 2.59 (br s), 2.29 (br s), 1.97 (br s), 1.56 (br s), 1.27 (br s), 0.97 (br m), 0.83 (br s); ¹³C NMR (100 MHz, CDCl₃) δ 174.0 (CO), 140.1, 137.9, 129.0, 128.6, 128.5, 126.9, 126.6, 125.6, 124.1, 64.9, 64.6, 35.3, 33.3, 32.8, 32.4, 32.0, 30.3, 29.9, 29.5, 28.3, 27.8, 26.9, 25.9, 13.5, 13.1, 12.9; IR spectrum (CDCl₃) 3027, 2958, 2925, 2855, 2046, 2027, 1995, 1977, 1941, 1737, 1666, 1605, 1564, 1455, 1379, 1246, 1217, 1162, 969, 851, 824, 758, 698 cm⁻¹; Mₙ = 4642, M_w = 9841, PDI = 2.12.
2-Phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (7c): 12% of 2-phenylethyl ester, 12% of 4-(2-hydroxyethyl)phenethyl ester and the rest (76%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (88% yield, 95.0 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.30-7.17 (br m), 5.39-5.10 (br m, internal -CH=CH-), 4.24 (br s), 3.80 (br s), 2.90 (br s), 2.83-2.80 (br m), 2.27 (br m), 1.98 (br s), 1.68 (br s), 1.58 (br s), 1.27 (br s), 0.98 (br m), 0.85-0.84 (br m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.1 (CO), 141.1, 138.0, 136.0, 129.3, 129.2, 129.0, 128.6, 126.7, 64.9, 63.7, 37.1, 36.7, 35.3, 34.9, 33.3, 32.8, 32.5, 32.1, 30.3, 29.9, 28.4, 27.8, 26.9, 26.0, 13.5, 13.2; IR spectrum (CDCl\(_3\)) 3418, 2927, 2856, 2049, 1980, 1940, 1734, 1666, 1565, 1515, 1498, 1454, 1383, 1251, 1170, 1032, 969, 757, 699, 645 cm\(^{-1}\); \(M_n = 3943, M_w = 9017, PDI = 2.29\).

2-Phenylethyl ester and pyrenyl methyl ester-containing modified polybutadiene (7h): 11% of 2-phenylethyl ester, 11% of pyrenyl methyl ester and the rest (78%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (84% yield, 91.3 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.27 (br s), 8.18-8.16 (br m), 8.07 (br m), 7.22 (br s), 5.83 (br s), 5.43-5.08 (br m, internal -CH=CH-), 4.27 (br s), 2.93 (br s), 2.58 (br s), 2.31 (br m), 1.96 (br s), 1.68 (br s), 1.57 (br s), 1.25 (br s), 0.97 (br m), 0.83 (br m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.1 (CO), 138.0, 131.8, 131.3, 130.8, 130.5, 129.6, 129.0, 128.6, 128.4, 128.2, 127.9, 127.5, 126.7, 126.2, 125.6, 125.5, 124.9, 124.7, 123.0, 64.9, 64.7, 36.7, 35.3, 32.8, 32.5, 32.1, 29.9, 28.3, 27.8, 23.1, 13.5, 13.1, 12.9, 12.0, 11.7; IR spectrum (CDCl\(_3\)) 2927, 2856, 2063, 1991, 1732, 1669, 1605, 1497, 1456, 1378, 1250, 1171, 1031, 969, 847, 768, 700, 667, 643, 623, 579, 520 cm\(^{-1}\); \(M_n = 4041, M_w = 8372, PDI = 2.07\).

2-Phenylethyl ester, heptyl ester and pyrenyl methyl ester-containing modified polybutadiene (8a): 9% of 2-phenylethyl ester, 9% of heptyl ester, 9% of pyrenyl methyl ester and the rest (73%) of internal olefins and saturated hydrocarbons based on terminal phenyl group (95% yield, 101.3 mg); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 8.29-8.22 (br m), 8.17-8.07 (br m), 7.29-7.24 (br m), 5.83 (br s), 5.39-5.11 (br m, internal -CH=CH-), 4.27 (br s), 4.04 (br s), 2.93 (br s), 2.59 (br s), 2.30 (br m), 2.00 (br s), 1.59 (br s), 1.29 cm\(^{-1}\).
(br s), 0.99 (br m), 0.90 (br m), 0.86 (br m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.1 (CO), 137.9, 131.7, 131.2, 130.7, 129.5, 128.9, 128.5, 127.8, 127.3, 126.6, 126.1, 125.5, 124.9, 124.6, 122.9, 64.8, 64.6, 64.5, 38.9, 37.1, 35.2, 33.2, 32.7, 32.4, 31.8, 29.8, 29.0, 28.7, 28.3, 27.7, 26.7, 26.0, 23.0, 22.7, 14.2; IR spectrum (CDCl$_3$) 3029, 2923, 2855, 2073, 2046, 2017, 1997, 1969, 1935, 1734, 1604, 1553, 1496, 1455, 1379, 1264, 1247, 1165, 1064, 1031, 1004, 969, 846, 739, 701, 682 cm$^{-1}$; $M_n = 4521$, $M_w = 10637$, PDI = 2.35.

**- Calculation of isolated yield of ester-containing modified polybutadiene**

<Calculation of isolated yield of 2-phenylethyl ester-containing modified polybutadiene ($6a$)>

Weight ratio can be calculated by $^1$H NMR spectroscopy.

For example, 2-phenylethyl ester-containing modified polybutadiene ($6a$) contains 28% of 2-phenylethyl ester and 72% of reduced or isomerized or internal olefin part. Molecular weight of ester monomer is 204.26 g/mol and the remaining part monomer is 54.09 g/mol.
The mole of 2-phenylethyl ester-containing modified polybutadiene (6a):

\[
\text{mole of 2-phenylethyl ester-containing modified polybutadiene (6a) (mmol)} = \frac{73.9 \text{ mg} \times 0.595}{(1800 \text{ mg/mmol} \times 0.45) + (15 \times 0.62 \times 149.16) \text{ mg/mmol}}
\]
\[
= \frac{43.9705 \text{ mg}}{810 \text{ mg/mmol} + 1387.188 \text{ mg/mmol}}
\]
\[
= \frac{43.9705 \text{ mg}}{2197.19 \text{ mg/mmol}} = 0.02001 \text{ mmol}
\]

\[
\text{mole of starting Polybutadiene (1) (mmol)} = \frac{50 \text{ mg}}{1800 \text{ mg/mmol}} = 0.02778 \text{ mmol}
\]

The yield of 2-phenylethyl ester-containing modified polybutadiene (6a):

\[
\text{yield of 2-phenylethyl ester-containing modified polybutadiene (6a) (%)} = \frac{0.02001 \text{ mmol}}{0.02778 \text{ mmol}} \times 100 = 72.03 \% \approx 72 \%
\]
$^1$H and $^{13}$C NMR SPECTRA

in CD$_2$Cl$_2$ (15/40)
Fig S1. HSQC spectrum of 6a in CDCl₃ was acquired on Bruker Advance II/DPX 400.
TGA and DSC thermograms

Fig S2. TGA plots of polybutadiene (1) and 2-phenylethyl ester-containing modified polybutadiene (6a)

Fig S3. DSC trace of polybutadiene (1) and 2-phenylethyl ester-containing modified polybutadiene (6a)