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Electronic Supplementary Information

Surface functionalization of silica using catalytic hydroesterification modified polybutadienes

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1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography was monitored using analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60 F-254) using UV light as a visualizing agent, *p*-anisaldehyde solution, and $KMnO_4$ solution as staining solutions, and heat as developing agent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance II/DPX 400 (400 MHz ^{1}H, 100 MHz ^{13}C) spectrometer with chemical shifts reported relative to residual deuterated solvent peaks. ^{1}H NMR spectra was referenced to residual CD_2Cl_2 (for ^{1}H, δ = 5.3 ppm), $CDCl_3$ (for ^{1}H, δ = 7.26 ppm) as internal standard, and is reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet). ^{13}C NMR spectra was referenced to the residual CD_2Cl_2 (54.00 ppm), $CDCl_3$ (77.26 ppm). Fluorescence spectra were obtained on a Perkin Elmer LS 55. Infrared spectra were obtained using a Nicolet Impact 400 spectrometer. Elemental analysis was obtained on a Thermo Finnigan Flash EA1112 at Sogang center for research facilities. Analytical GPC was performed on a JASCO HPLC equipped with KF-404HQ columns (ID. 4.6 X L. 250nm, Shodex, Tokyo, Japan) using THF as a eluent at a flow rate of 1.0 mL/min.

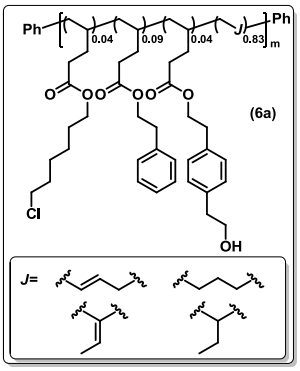
2. Materials

Reagent grade chemicals, sodium formate (**2**), 2-phenylethyl alcohol (**3a**), 2,2'-(1,4-phenylene)diethanol (**3b**), 6-chlorohexylalcohol (**3c**), pyrenylmethanol (**3d),** $Ru_3(CO)_{12}$ (**4**), 2-pyridinemethanol (**5**), 4-dimethylaminopyridine (**11**), trifluoromethanesulfonic acid (TfOH, **14**), sodium azide, copper sulfate, sodium ascorbate, nitrobenzene were purchased from Aldrich Chemical Company and Alfa Aesar and used as received without further purification unless otherwise stated. Tetrahydrofuran (THF), 1,4-dioxane, and *N*,*N*-dimethylformamide (DMF) were distilled before use. Polybutadiene (**1**) was purchased from Aldrich and its molecular weight was determined to be 1,800 with PDI(M_w/M_n) = 2.16. Silicana noparticle (**13**, particle size: 100 nm) was purchased from Fuji silysia chemical. 4-(dimethylamino)azobenzene-4'-sulfonamide (DABS) linked acetylene **8** was prepared by reaction between the 4-(4-Dimethylaminophenylazo)benzenesulfonyl chloride and propargylamine.

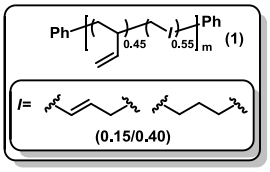
3. Experimental

3.1. Preparation of 6-chloro-1-hexyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6a, eqn (1))

A 5 mL pressure vial was charged with polybutadiene (**1**, 50 mg, 0.416 mmol of vinyl group), sodium formate (**2**, 0.832 mmol), 2-phenylethyl alcohol (**3a**, 0.445 mmol), 2,2'-(1,4-phenylene)diethanol (**3b,** 0.197 mmol), 6-chlorohexanol (**3c,** 0.197 mmol), $Ru_3(CO)_{12}$ (**4**, 0.0210 mmol), 2-pyridinemethanol (**5**, 0.0832 mmol) and 1,4-dioxane (1 mL). The mixture was stirred at 150 ^oC for 12 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 multi-functionalized polybutadiene **6a** (70% yield, 51 mg); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.27-7.14 (br m), 5.37-5.07 (br m, internal –CH=CH-), 4.22 (br s), 4.00 (br s), 3.77 (br s), 3.53-3.50 (br m), 2.89 (br s), 2.80-2.77 (br m), 2.57 (br s), 2.24 (br s), 1.95 (br s), 1.76-1.73 (br m), 1.64 (br s), 1.54 (br s), 1.43-1.41 (br m), 1.24 (br s), 0.95 (br s), 0.82-0.81 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.2 (CO), 139.7, 138.7, 137.9, 136.5, 129.8, 129.5, 129.0, 127.1, 65.3, 64.0, 54.5, 54.3, 54.0, 53.7, 53.5, 45.5, 40.0, 39.6, 37.7, 37.2, 36.7, 35.8, 35.4, 33.8, 33.3, 33.2, 32.5, 30.8, 30.5, 29.2, 28.9, 28.4; IR (neat): 3456, 3026, 2958, 2924, 2854, 2362, 2046, 2024, 1974, 1942, 1737, 1663, 1604, 1569, 1515, 1497, 1457, 1378, 1264, 1165, 1051, 969, 885, 813, 741, 699, 587, 568, 496 cm^{-1}; M_w/M_n = 3.1724.



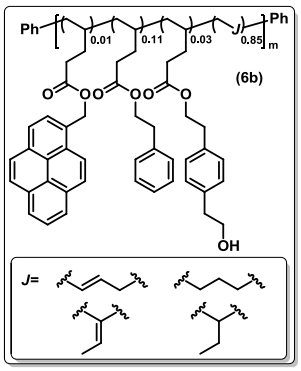
- Phenyl terminated polybutadiene (1): ^1H NMR (400 MHz, CD_2Cl_2) δ 7.24-7.21 (br m), 7.15-7.13 (br m), 5.83-5.74 (br m, terminal –CH=CH-), 5.57-5.55 (br m), 5.36-5.35 (br m, internal –CH=CH-), 5.03-4.86 (br m, terminal –CH=CH-), 2.65-2.59 (br m), 2.51-2.50 (br m), 2.36-2.28 (br m), 2.05-2.01 (br m), 1.79-1.26 (br m), 1.00-0.96 (br m), 0.89-0.83 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 145.2, 144.9, 144.4, 143.7, 143.4, 132.4, 132.0, 131.2, 130.8, 130.7, 130.5, 130.3, 130.1, 130.0, 129.1, 128.9, 128.5, 128.4, 126.3, 114.9, 114.5, 113.5, 112.5, 112.3, 54.5, 54.3, 54.0, 53.7, 53.5, 46.0, 44.4, 44.2, 43.1, 42.3, 41.9, 41.5, 41.3, 41.1, 40.0, 39.9, 39.0, 38.7, 38.2, 37.6, 36.8, 36.3, 36.1, 35.6, 34.7, 34.2, 34.1, 33.5, 33.1, 32.7, 32.1, 30.9, 28.3, 28.1, 26.3, 25.8, 25.7, 6.99; IR (neat): 3076, 2999, 2972, 2918, 2855, 1639, 1453, 1417, 994, 968, 909, 747, 699 cm^{-1}; M_w/M_n = 2.16.



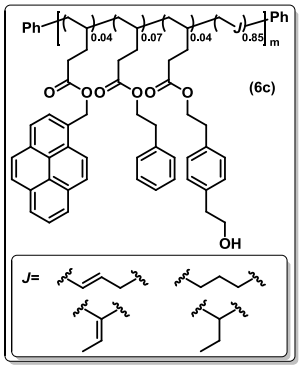
3.2. A typical procedure for synthesis of pyrene-modified polybutadiene (Table 1, entry 1-7)

A 5 mL pressure vial was charged with polybutadiene (**1**, 50 mg, 0.416 mmol of vinyl group), sodium formate (**2**, 0.832 mmol), pyrenylmethanol (**3d**, 0.0832 mmol), 2-phenylethyl alcohol (**3a**, 0.588 mmol), 2,2'-(1,4-phenylene)diethanol (**3b,** 0.168 mmol), $Ru_3(CO)_{12}$ (**4**, 0.0210 mmol), 2-pyridinemethanol (**5**, 0.0832 mmol) and 1,4-dioxane (1 mL). The mixture was stirred at 150 ^oC for 12 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 modified polymer **6b** containing 1:7:2 ratio of corresponding pyrenylmethyl, 2-phenylethyl, and 4-(2-hydroxyethyl)phenethyl esters (72% yield, 50.3 mg).

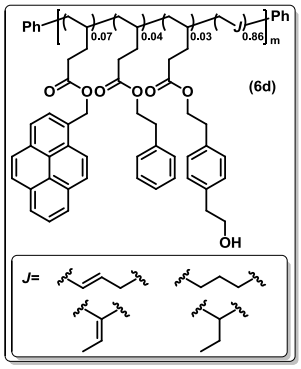
- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6b): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.27 (br s), 8.20-8.15 (br m), 8.07-8.02 (br m), 7.27-7.14 (br m), 5.80 (br s), 5.35-5.07 (br m, internal –CH=CH-), 4.23 (br s), 3.78 (br s), 2.90 (br s), 2.81-2.77 (br m), 2.57-2.55 (br m), 2.25 (br s), 1.96 (br s), 1.65 (br s), 1.55 (br s), 1.25 (br s), 0.95 (br s), 0.83-0.81 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.3 (CO), 138.8, 137.7, 136.7, 129.6, 129.0, 127.1, 126.1, 125.5, 125.2, 65.3, 64.1, 53.5, 39.5, 38.8, 37.2, 36.8, 35.8, 35.4, 33.9, 32.5, 30.7, 30.4, 28.9, 28.3, 27.4, 26.5, 13.7, 13.1, 12.1, 11.3; IR (neat): 3456, 2958, 2924, 2854, 2362, 2341, 2046, 2026, 1975, 1944, 1737, 1649, 1605, 1454, 1378, 1264, 1162, 1052, 969, 882, 846, 818, 741, 699 cm^{-1}; M_w/M_n = 3.1282.



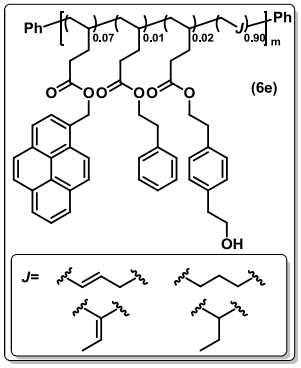
- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6c): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.27 (br s), 8.20-8.15 (br m), 8.07-8.02 (br m), 7.27-7.15 (br m), 5.80 (br s), 5.37-5.07 (br m, internal –CH=CH-), 4.22 (br s), 3.78 (br s), 2.88 (br s), 2.79 (br s), 2.57 (br s), 2.26 (br s), 1.97 (br s), 1.66 (br s), 1.55 (br s), 1.26 (br s), 0.96 (br s), 0.82 (br s); *Mw*/*Mn* = 2.5399.



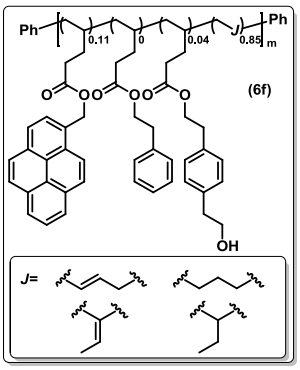
- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6d): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.26 (br s), 8.19-8.14 (br m), 8.06-8.02 (br m), 7.26-7.15 (br m), 5.80 (br s), 5.36-5.09 (br m, internal –CH=CH-), 4.23 (br s), 3.78 (br s), 2.88 (br s), 2.79 (br s), 2.56 (br s), 2.26 (br s), 1.97 (br s), 1.66 (br s), 1.56 (br s), 1.26 (br s), 0.97 (br s), 0.83 (br s); *Mw*/*Mn* = 2.6555.



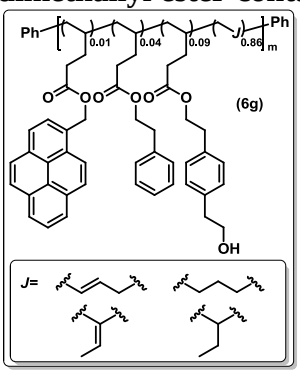
- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6e): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.26 (br s), 8.19-8.13 (br m), 8.05-8.03 (br m), 7.23-7.15 (br m), 5.80 (br s), 5.35-5.07 (br m, internal –CH=CH-), 4.23 (br s), 3.77 (br s), 2.88 (br s), 2.79 (br s), 2.57 (br s), 2.30 (br s), 1.97 (br s), 1.67 (br s), 1.56 (br s), 1.26 (br s), 0.97 (br s), 0.83 (br s); M_w/M_n = 2.6485.



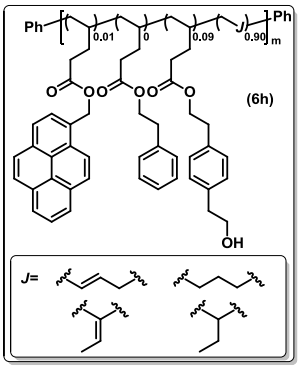
- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6f): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.32 (br s), 8.18-8.12 (br m), 8.03-8.00 (br m), 7.23-7.15 (br m), 5.80 (br s), 5.35-5.07 (br m, internal –CH=CH-), 4.23 (br s), 3.77 (br s), 2.88 (br s), 2.79 (br s), 2.57 (br s), 2.30 (br s), 1.98 (br s), 1.68-1.56 (br m), 1.27 (br s), 0.98 (br s), 0.84 (br s); *Mw*/*Mn* = 2.6551.



- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6g): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.27 (br s), 8.20-8.15 (br m), 8.07 (br s), 7.27-7.14 (br m), 5.80 (br s), 5.36-5.07 (br m, internal –CH=CH-), 4.21 (br s), 3.77 (br s), 2.87 (br s), 2.80-2.77 (br m), 2.57-2.55 (br m), 2.25 (br s), 1.96 (br s), 1.65 (br s), 1.55 (br s), 1.25 (br s), 0.95 (br s), 0.83-0.81 (br m); *Mw*/*Mn* = 2.7513.

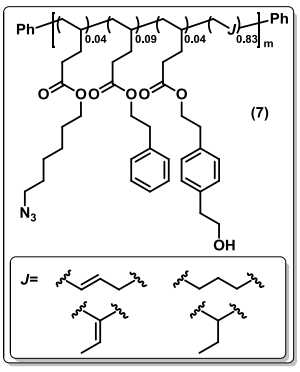


- Pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (6h): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.20 (br s), 8.17-8.15 (br m), 8.07 (br s), 7.23-7.14 (br m), 5.80 (br s), 5.35-5.07 (br m, internal –CH=CH-), 4.21 (br s), 3.77 (br s), 2.87 (br s), 2.80-2.77 (br m), 2.57 (br s), 2.25 (br s), 1.96 (br s), 1.65 (br s), 1.55 (br s), 1.25 (br s), 0.95 (br s), 0.83-0.81 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.3 (CO), 138.8, 136.6, 129.7, 129.6, 128.9, 126.1, 125.2, 65.3, 64.1, 39.5, 35.3, 33.8, 32.3, 30.4, 28.9, 13.1; IR (neat): 3426, 2923, 2854, 2362, 2342, 1975, 1735, 1458, 1380, 1275, 1261, 1164, 1049, 969, 764, 750 cm^{-1}; M_w/M_n = 3.3120.

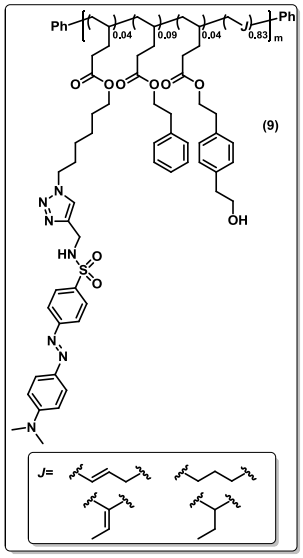


3.3. Preparation of polymer modified silica nanoparticle (Fig. 2)

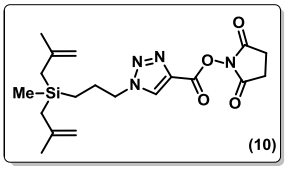
- Preparation of 6-azido-1-hexyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl dimethallyl ester-containing modified polybutadiene (7): A solution of 6-chloro-1-hexyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (**6a**) (51 mg, 0.026 mmol based on the amount of 6-chloro-1-hexyl ester) and sodium azide (0.26 mmol) in DMF/THF (135 μL/109 μL) was stirred at 100 ºC for 12 h. After addition of saturated aqueous NH_4Cl and dichloromethane, the organic layer was separated and the aqueous layer was extracted with dichloromethane 3 times. The combined organic layers were dried over anhydrous $MgSO_4$,



filtered, and concetrated in vacuo. The residue was separated and the aqueous layer was extracted with di chloromethane 3 times. The combined organic layers were washed throughly with methanol and dried to give 6-azido-1-hexyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modifie d polybutadiene (**7,** 57% yield, 29.1 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.22-7.15 (br m), 5.08 (br m, int ernal –CH=CH-), 4.23 (br s), 4.02 (br s), 3.78 (br s), 3.25 (br s), 2.89-2.80 (br m), 2.58 (br s), 2.27 (br s), 1.98 (br s), 1.56 (br s), 1.26 (br s), 0.96-0.84 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.3 (CO), 141.5, 1 39.9, 138.7, 137.8, 136.6, 130.9, 129.7, 129.5, 129.0, 128.8, 127.0, 65.2, 64.1, 54.5, 54.4, 54.3, 54.0, 53.7, 53.5, 52.0, 39.5, 39.0, 37.6, 37.2, 36.6, 35.7, 35.4, 34.7, 338., 33.3, 32.9, 32.4, 31.2, 30.7, 30.4, 29.4, 29. 2; IR (neat): 3417, 2925, 2855, 2361, 2342, 2251, 2096, 1989, 1736, 1672, 1605, 1514, 1496, 1459, 1378, 1262, 1167, 1052, 969, 910, 820, 734, 699, 648, 570, 496 cm^{-1}; M_w/M_n = 3.2519.

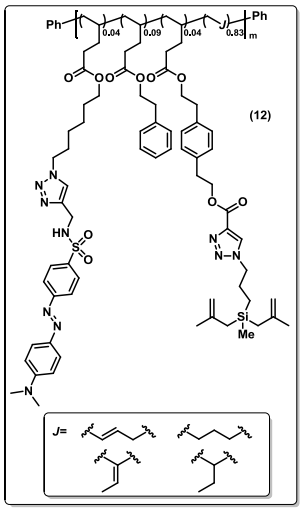


- Diazo group, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-co ntaining modified polybutadiene (9): 6-azido-1-hexyl ester, 2-phenylethyl este r and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (**7**) (29.1 mg, 0.015 mmol based on the amount of 6-azido-1-hexyl ester) and a mixt ure of $CuSO_4 \cdot 5\ H_2O$ (0.0015 mmol) and sodium ascorbate (0.003 mmol) in wate r were added to a solution of crude Dabsyl (**8**, 0.030 mmol) in THF. The mixture was stirred at 100 ^{o}C for 12 h. After addition of saturated NH_4Cl aqueous soluti on and dichloromethane, the organic layer was separated extracted 3 times and t he aqueous layer was extracted with dichloromethane 3 times. The combined or ganic layers were dried over anhydrous $MgSO_4$, filtered, and concetrated in vac uo. The residue was washed throughly with methanol and dried to give diazo gr oup, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (**9,** 64% yield, 22 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86 (br s), 7.26-7.13 (br m), 6.76-6.74 (br m), 5.3 0-5.07 (br m, internal –CH=CH-), 4.22 (br s), 4.00-3.93 (br m), 3.77 (br s), 3.08(br s), 2.88 (br s), 2.78 (br s), 2.56 (br s), 2.24 (br s), 1.95 (br s), 1.74 (br s), 1.65 (br s), 1.53 (br s), 1.24 (br s), 0.94 (br s), 0.82-0.80 (br m); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.1 (CO), 156.1, 153.8, 144.0, 141.5, 139.5, 138.7, 137.7, 136. 6, 135.5, 130.9, 129.7, 129.5, 129.0, 128.7, 127.0, 126.2, 123.0, 112.0, 65.2, 64.1, 54.5, 54.3, 54.0, 53.7, 53.5, 41.8, 40.7, 39.5, 35.7, 35.3, 33.7, 32.4, 30.7, 30.4, 28.8, 27.9, 27.3, 26. 5, 23.5; IR (neat): 3288, 2923, 2853, 2361, 2341, 1733, 1676, 1603, 1456, 1366, 1262, 1165, 1136, 1092, 843, 748, 699, 654 cm^{-1}; M_w/M_n = 1.9878.



2,5-dioxopyrrolidin-1-yl1-(3-(methylbis(2-methylallyl)sillyl)propyl)-1H-1, 2,3-triazole-4-carboxylate (10) [CAS No. 1235552-40-5]: To a solution of so

dium ascorbate (0.66 mmol) in water was added $CuSO_4 \cdot 5\ H_2O$ (0.33 mmol), causing a change in color fr om dark brown to yellow orange. The resulting mixture was added to a solution of 2-propyonic acid (6.6 mmol), 3-azidopropyldimethallylsilane (4.2 mmol) in THF (17 mL). The mixture was stirred at room tem perature for 12 h and then diluted with water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo giving a residue that was subjected to silica column chromatography, giving pure **10** (n-hexane:ethyl acetate=1:1) (white solid, 44% yield, 0.75 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 4.61 (s, 2H), 4.48 (s, 2H), 4.42 (t, J = 7.16 Hz, 2H), 2.91 (s, 4 H), 2.01-1.93 (m, 2H), 1.69 (s, 6H), 1.58 (s, 4H), 0.60-0.56 (m, 2H), 0.07 (s, 3H); ^{13}C NMR (100MHz, C DCl_3) δ 169.2, 155.9, 143.0, 134.7, 129.3, 129.2, 109.5, 54.0, 25.8, 25.7, 25.5, 25.2, 11.0, -4.24.



- Diazo group, 2-phenylethyl ester and dimethallyl silane group containing modified polybutadiene (12): A mixture of diazo group, 2-phenylethyl ester an d 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (**9**, 22 mg, 0.0095 mmol based on the amount of 4-(2-hydroxyethyl)phenethyl ester), N HS-ester-functionalized methallylsilane (**10**, 0.033 mmol) and 4-DMAP (**11**, 0. 0095 mmol) in dichloromethane was stirred at 100 ^oC for 12 h. After addition of saturated NH_4Cl aqueous solution and dichloromethane, organic layer separated and the aqueous layer was extracted with dichloromethane 3 times. The combin ed organic layers were dried over anhydrous $MgSO_4$, filtered, and concetrated in vacuo. The residue was then washed throughly with methanol and dried to give diazo group, 2-phenylethyl ester and dimethallyl silane group containing modified polybutadiene (**1 2**, 82% yield, 20.3 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86-7.85 (br m), 7.26-7.13 (br m), 6.75-6.73 (br m), 5.30-5.06 (br m, internal –CH=CH-), 4.45 (br s), 4.32 (br s), 4.21 (br s), 3.93(br s), 3.08 (br s), 3.01(b r s), 2.88-2.85 (br m), 2.77 (br s), 2.56 (br s), 2.23 (br s), 1.94 (br s), 1.80 (br s), 1.73-1.70 (br m), 1.66 (br s), 1.53 (br s), 1.23 (br s), 0.94 (br s), 0.80 (br s), 0.56 (br s), 0.12- -0.009 (br m); ^{13}C NMR (100MHz, C D_2Cl_2) δ 174.2 (CO), 153.8, 144.1, 138.8, 137.7, 136.6, 130.9, 129.7, 129.6, 129.5, 129.0, 128.8, 127.0, 1 26.3, 124.8, 124.2, 123.0, 112.0, 65.7, 65.2, 64.5, 64.1, 4.5, 54.3, 54.0, 53.7, 53.5, 40.7, 39.5, 35.7, 35.4, 3 3.9, 33.3, 32.5, 30.6, 30.4, 29.2, 28.9, 28.3, 27.4, 27.1, 26.8, 26.7, 26.5, 26.2, 25.9, 25.8, 14.6; IR (neat): 2 924, 2854, 2361, 2341, 1736, 1603, 1521, 1457, 1364, 1276, 1259, 1166, 1136, 1089, 969, 822, 764, 750, 699, 598 cm^{-1}; M_w/M_n = 2.3360.

- Preparation of 12 modified silica nanoparticle (15)

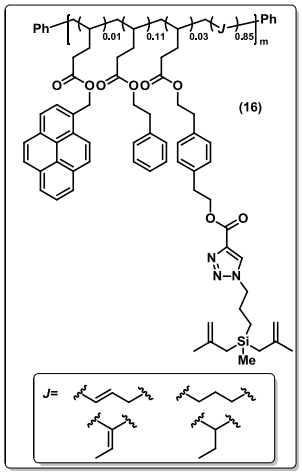
A 1 mL pressure vial was charged with silica nanoparticle (**13**, 50 mg), **12** (1, 3, 5, 8, 10, 20, and 40 mg), TfOH (**14**, 5 mol% based on **12**) and dichloromethane (700 μL). The mixture was stirred at room

temperature for 12 h and filtered, giving a solid that was washed with dichloromethane and acetone. The resulting solid was dried in vacuo to give **15** with different extents of loading.

$$Loading\ rate\ (\frac{mmol}{g}) = \frac{(\text{EA value}) \times 10}{(\text{Number of atoms}) \times (Atomic\ weight)}$$

Result value of **15**	EA value		Loading rate (mmol/g)		UV
Amount of **12**	C	N	C	N	497 nm A.
1 mg	1.41	0.018	0.017	0.0013	0.035
3 mg	2.36	0.081	0.028	0.0058	0.075
5 mg	3.91	0.18	0.047	0.013	0.13
8 mg	4.86	0.26	0.058	0.019	0.19
10 mg	6.33	0.41	0.075	0.029	0.31
20 mg	9.23	0.73	0.11	0.052	0.38
40 mg	13.74	1.25	0.16	0.089	0.27

3.4. Measurements of fluorescence of nitrobenzene (Fig. 4)



- Pyrenyl methyl ester, 2-phenylethyl ester and dimethallyl silane group con taining modified polybutadiene (16): A solution of pyrenyl methyl ester, 2-phenylethyl ester and 4-(2-hydroxyethyl)phenethyl ester-containing modified polybutadiene (**6b**, 50.3 mg, 0.020 mmol), NHS-ester-functionalized methallylsilane (**10**, 0.070 mmol) and 4-DMAP (**11**, 0.020 mmol) in dichloromethane was stirred at 100 ºC for 12. After addition of saturated NH_4Cl aqueous solution and dichloromethane, organic layer was extracted 3 times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered, and concetrated in vacuo. The precipitate was then washed throughly with methanol and dried to pyrenyl methyl ester, 2-phenylethyl ester and dimethallyl silane group containing modified polybutadiene (**16**, 82% yield, 46.1 mg); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.27 (br s), 8.19-8.15 (br m), 8.06-8.00 (br m), 7.27-7.14 (br m), 5.80 (br s), 5.35-5.07 (br m, internal –CH=CH-), 4.59 (br s), 4.46 (br s), 4.32-4.31 (br m), 4.22 (br s), 3.03 (br s), 2.90-2.88 (br m), 2.77 (br s), 2.66-2.55 (br m), 2.24 (br s), 1.95 (br s), 1.73-1.67 (br m), 1.57-1.55 (br m), 1.24 (br s), 0.95 (br s), 0.81 (br s), 0.58-0.53 (br m), 0.048 (br s); ^{13}C NMR (100MHz, CD_2Cl_2) δ 174.1 (CO), 169.8, 161.1, 143.5, 140.3, 138.7, 137.1, 136.5, 132.3, 131.7, 130.8, 129.5, 129.0, 127.0, 126.0, 125.0, 109.6, 66.2, 65.2, 35.7, 35.3, 33.8, 32.9, 32.4, 30.4, 28.8, 26.3, 26.0, 15.8, 25.6, 13.5, 13.1; IR (neat): 3444, 3054, 3028, 2925, 2855, 2728, 2306, 2060, 1988, 1813, 1737, 1672, 1638, 1605, 1543, 1516, 1497, 1456, 1377, 1265, 1226, 1205, 1169, 1073, 1047, 1014, 971, 873, 844, 819, 738, 701, 649, 570, 496, 429 cm^{-1}; *Mw*/*Mn* = 3.6243.

- Preparation of 16 modified silica nanoparticle (17)

A 1 mL pressure vial was charged with silica nanoparticle (**13**, 50 mg), **16** (10 mg), TfOH (**14**, 5 mol% based on **16**) and dichloromethane (700 μL). The mixture was stirred at room temperature for 12 h, and filtered to give a solid that was washed with dichloromethane and acetone. The resulting solid was dried in vacuo to give **17**.

- Fluorescence spectra of 17 at different concentration of nitrobenzene (Fig. 4b)

Before addition of nitrobenzene, the fluorescence spectrum of **17** (0.125 mg in 2mL CH_2Cl_2) was recorded (excitation at 330 nm). Then, 2 μL to 2 mL of a solution of nitrobenzene (0.04 mM) in dichloromethane was added and fluorescent spectra of the mixture was recorded (Fig. 3a). This procedure was repeated using 2 mL of the nitrobenzene solution.

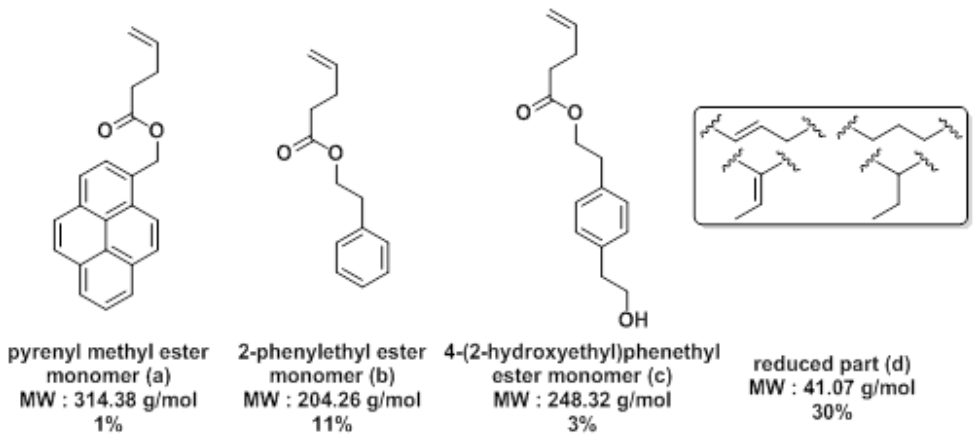
- Recycling experiment of 17 with addition of nitrobenzene (Fig. 4c)

Before addition of nitrobenzene, the fluorescence spectrum of **17** (0.25 mg in 2 mL CH_2Cl_2) was recorded (excitation at 330 nm). This was followed by addition of 2 μL nitrobenzene, and the fluorescence spectrum was measured. The mixture was subjected to centrifugation and washed with dichloromethane (1 mL for 3 times), and the fluorescence spectrum was measured. This procedure was repeated 5 times.

3.5. Calculation of isolated yield of ester-containing modified polybutadiene

<Calculation of isolated yield of **6b**>

Weight ratio can be calculated by ^{1}H NMR spectroscopy. For example, Modified polybutadiene (**6b**) contains 1% of pyrenyl methyl ester, 11% of 2-phenylethyl ester, 3% of 4-(2-hydroxyethyl)phenethyl ester 30% of reduced part and 55% of isomerized of internal olefin part. Molecular weight of pyrenyl methyl ester monomer is 314.38 g/mol, 2-phenylethyl ester monomer is 204.26 g/mol, 4-(2-hydroxyethyl)phenethyl ester monomer is 248.32 g/mol and reduced part monomer is 41.07 g/mol.



Weight of product polymer

Weight ratio can be calculated by ^{1}H NMR spectroscopy

$$Mole\ of\ each\ part(mmol) = \frac{A\ mg \times (Weight\ ratio\ of\ ester\ in\ modified\ polybutadiene)}{(Molecular\ weight\ of\ ester\ monomer)}$$

$$Weight\ ratio\ of\ \boldsymbol{a}\ in\ modified\ polybutadiene$$
$$= \frac{314.38\ g/mol \times 0.01}{(314.38\ g/mol \times 0.01) + (204.26\ g/mol \times 0.11)(248.32\ g/mol \times 0.03)(41.07\ g/mol \times 0.30)(54.09\ g/mol \times 0.55)}$$
$$= 0.042$$

$$The\ mole\ of\ \boldsymbol{a}\ (mmol) = \frac{50.3\ mg \times 0.042}{314.38\ g/mol} = 0.0067\ mmol$$

$$Total\ mole\ of\ modified\ polybutadiene\ (mmol)$$
$$= (Mole\ of\ \boldsymbol{a}) + (Mole\ of\ \boldsymbol{b}) + (Mole\ of\ \boldsymbol{c}) + (Mole\ of\ \boldsymbol{d})$$
$$= 0.0067\ mmol + 0.074\ mmol + 0.020\ mmol + 0.20\ mmol$$
$$= 0.30\ mmol$$

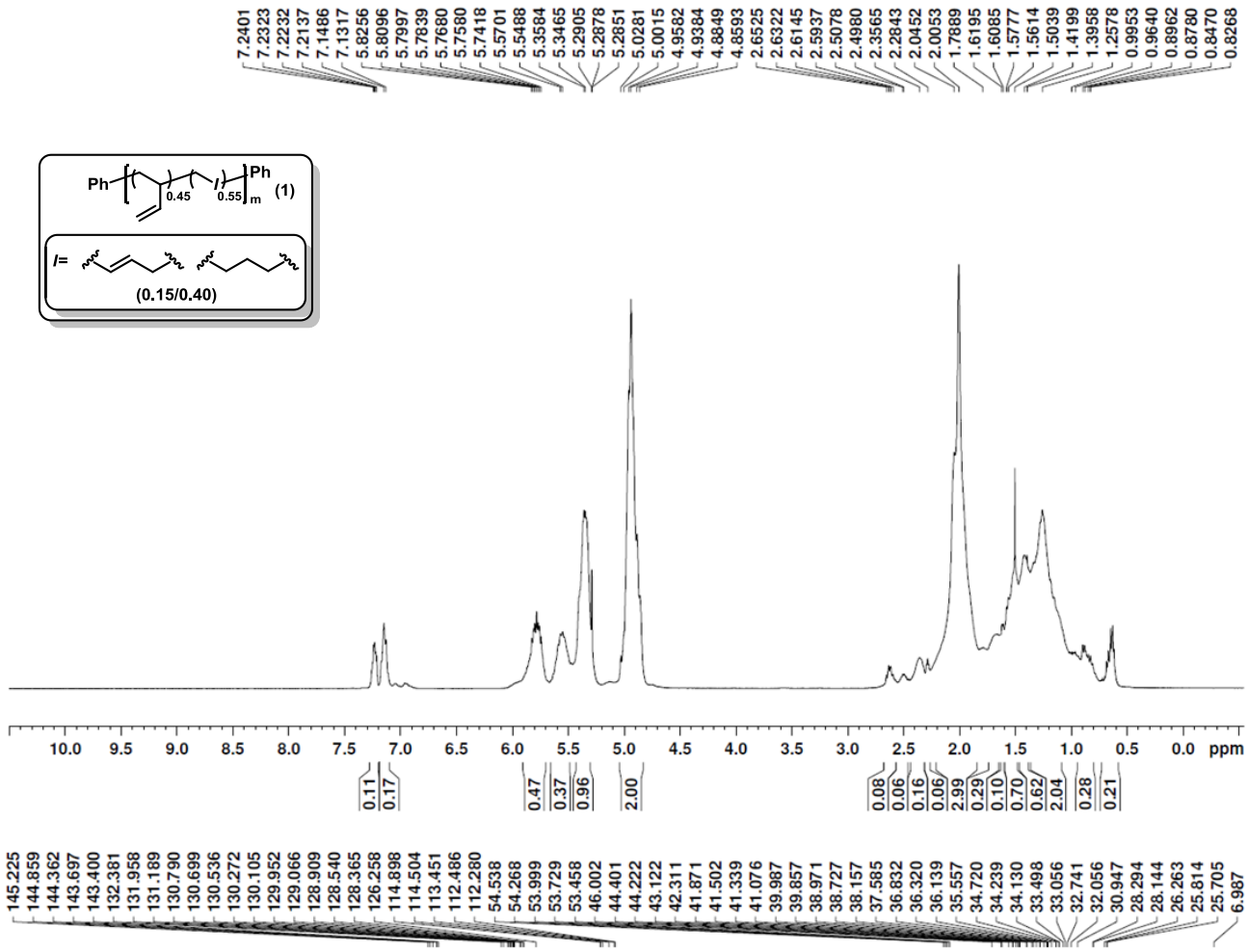
The yield of **6b**:

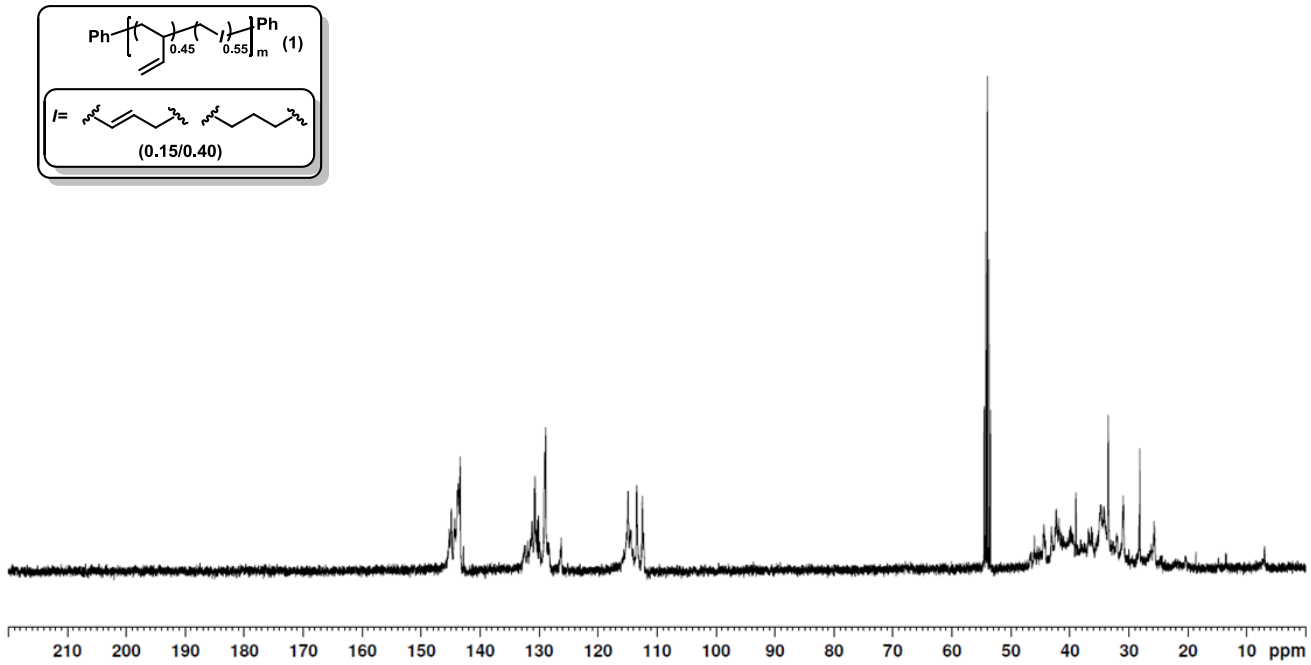
$$Mole\ \text{of starting polybutadiene}\ (\mathbf{1})\ (mmol) = \frac{50\ mg \times 0.45}{54.09\ g/mol} = 0.42\ mmol$$

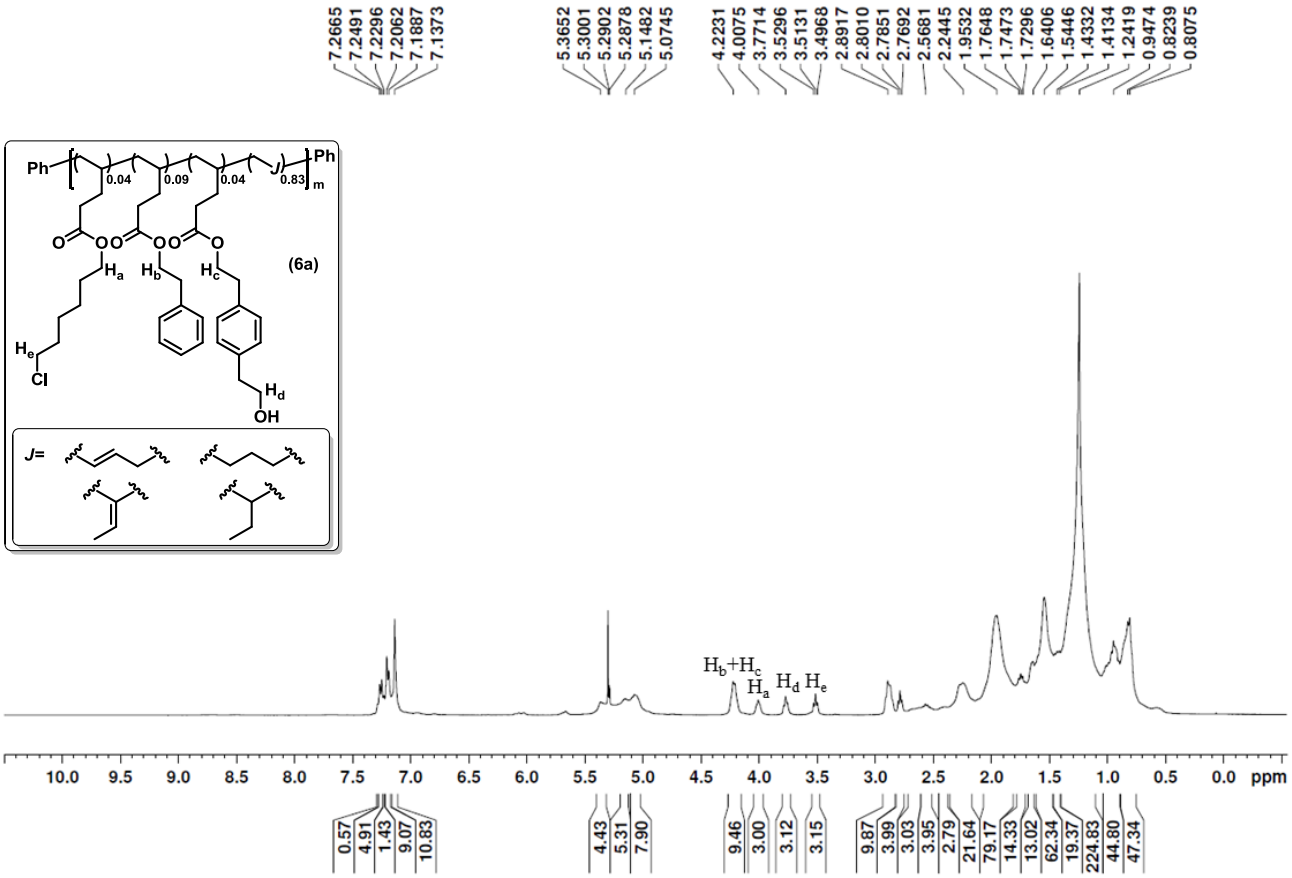
terminal alkyne monomer
Molecular Weight: 54.09 g/mol
45%

$$Yield\ \text{of}\ \boldsymbol{a}\ (\%) = \frac{0.30\ mmol}{0.42\ mmol} \times 100 = 71\%$$

4. ^{1}H and ^{13}C NMR SPECTRA



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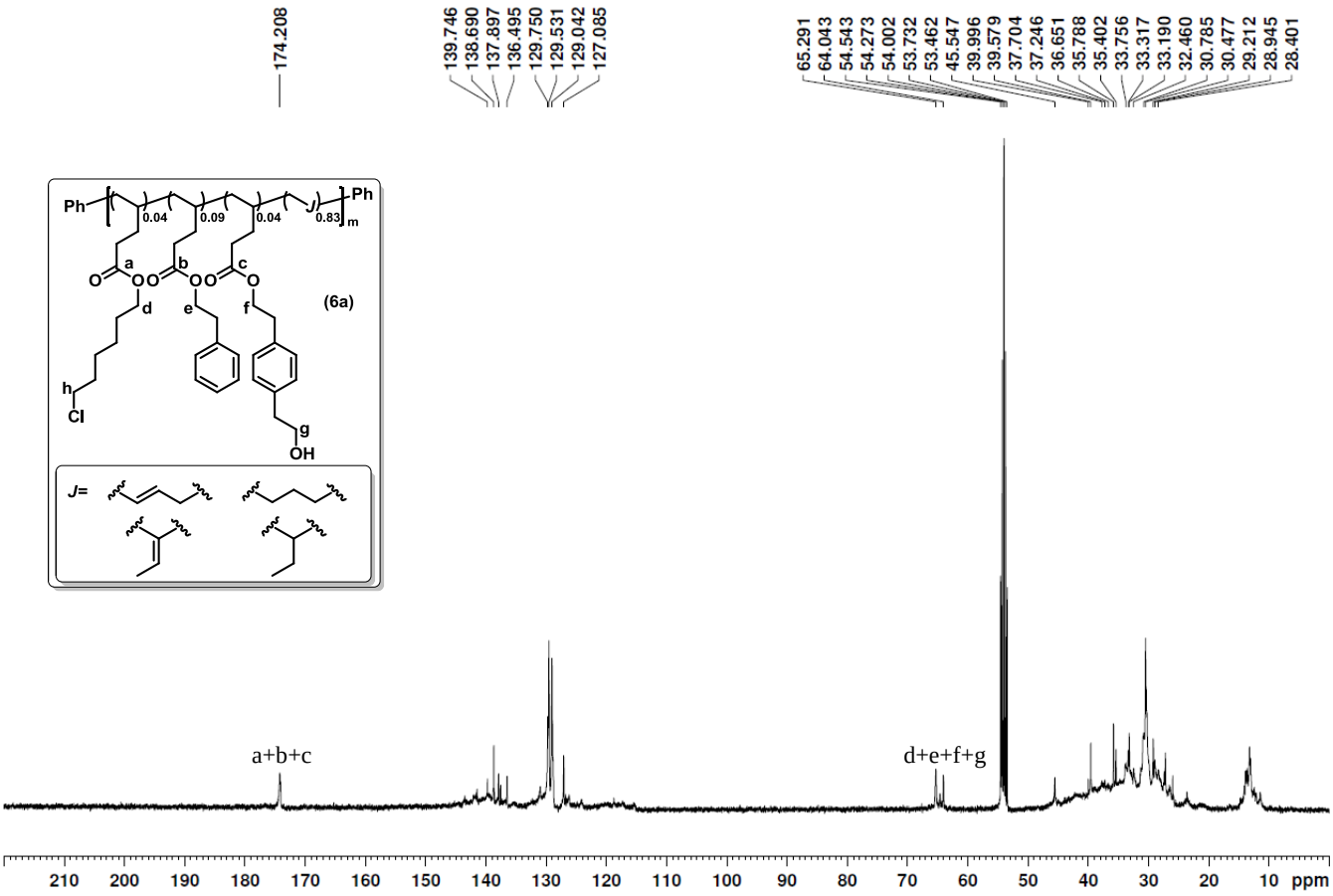
5.3652 5.3001 5.2902 5.2878 5.1482 5.0745
4.2231 4.0075 3.7714 3.5296 3.5131 3.4968 2.8917 2.8010 2.7851 2.7692 2.5681 2.2445 1.9532 1.7648 1.7473 1.7296 1.6406 1.5446 1.4332 1.4134 1.2419 0.9474 0.8239 0.8075
Ph
0.04
0.09
0.04
0.83
m
Ph
(6a)
Ha
Hb
Hc
He
Cl
Hd
OH
J=
Hb+Hc
Ha
Hd
He
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.57 4.91 1.43 9.07 10.83
4.43 5.31 7.90
9.46 3.00 3.12 3.15
9.87 3.99 3.03 3.95 2.79 21.64 79.17 14.33 13.02 62.34 19.37 224.83 44.80 47.34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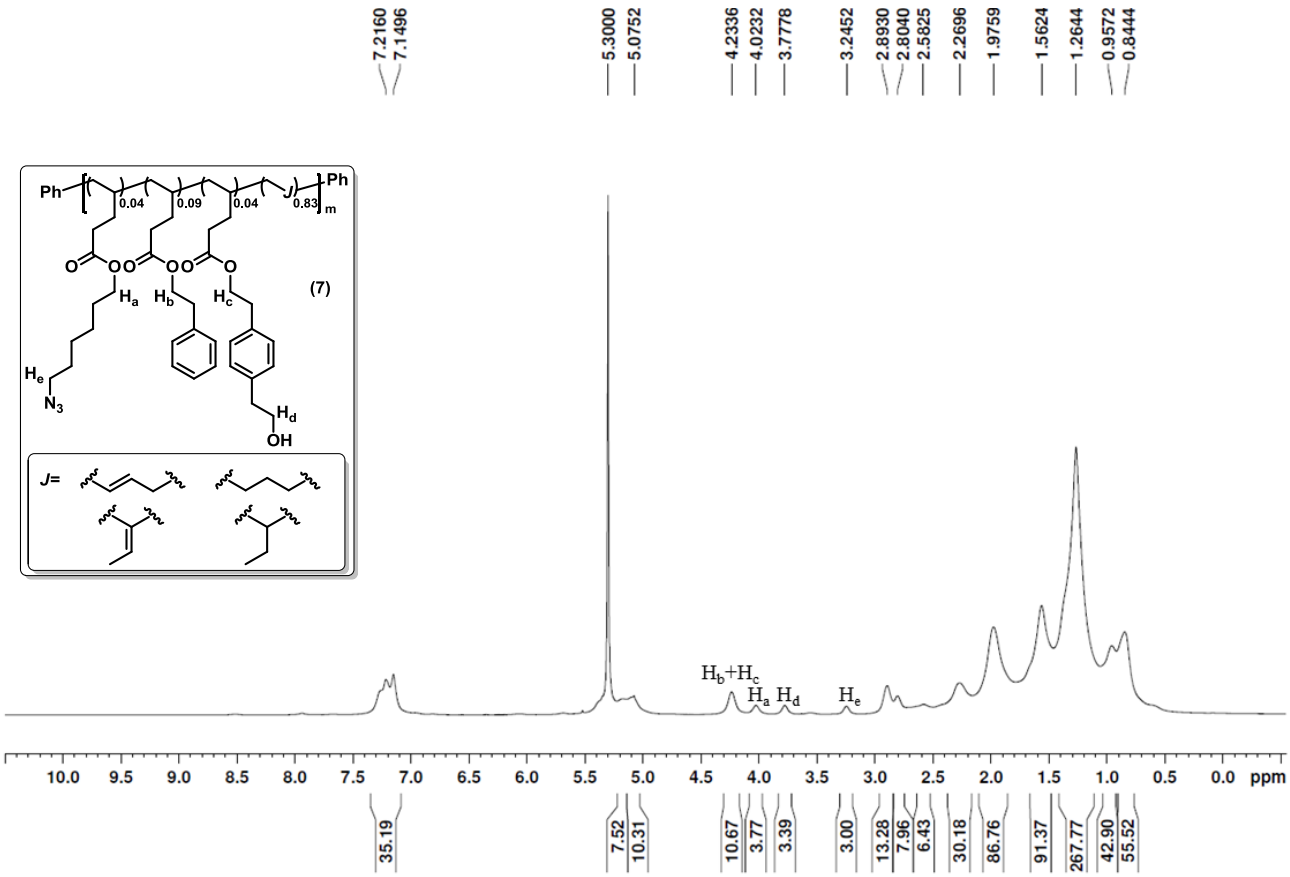
139.746 138.690 137.897 136.495 129.750 129.531 129.042 127.085
65.291 64.043 54.543 54.273 54.002 53.732 53.462 45.547 39.996 39.579 37.704 37.246 36.651 35.788 35.402 33.756 33.317 33.190 32.460 30.785 30.477 29.212 28.945 28.401
Ph
0.04
0.09
0.04
0.83
m
Ph
a
b
c
d
e
f
(6a)
h
Cl
g
OH
J=
a+b+c
d+e+f+g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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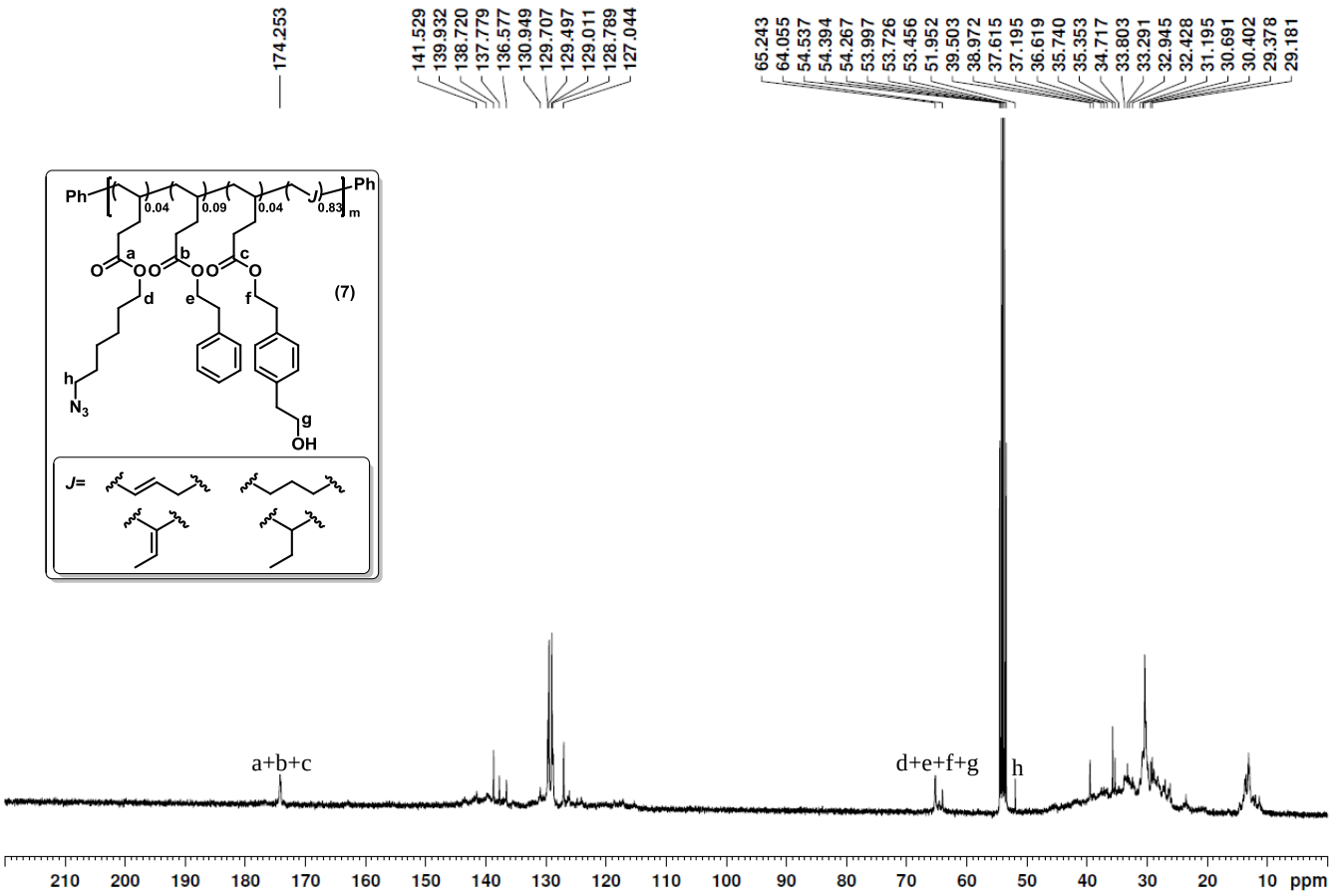
7.1496
5.3000
5.0752
4.2336
4.0232
3.7778
3.2452
2.8930
2.8040
2.5825
2.2696
1.9759
1.5624
1.2644
0.9572
0.8444
Ph
0.04
0.09
0.04
0.83
m
Ph
(7)
H_a
H_b
H_c
H_d
H_e
N_3
OH
J=
H_b+H_c
H_a
H_d
H_e
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
35.19
7.52
10.31
10.67
3.77
3.39
3.00
13.28
7.96
6.43
30.18
86.76
91.37
267.77
42.90
55.52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139.932
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136.577
130.949
129.707
129.497
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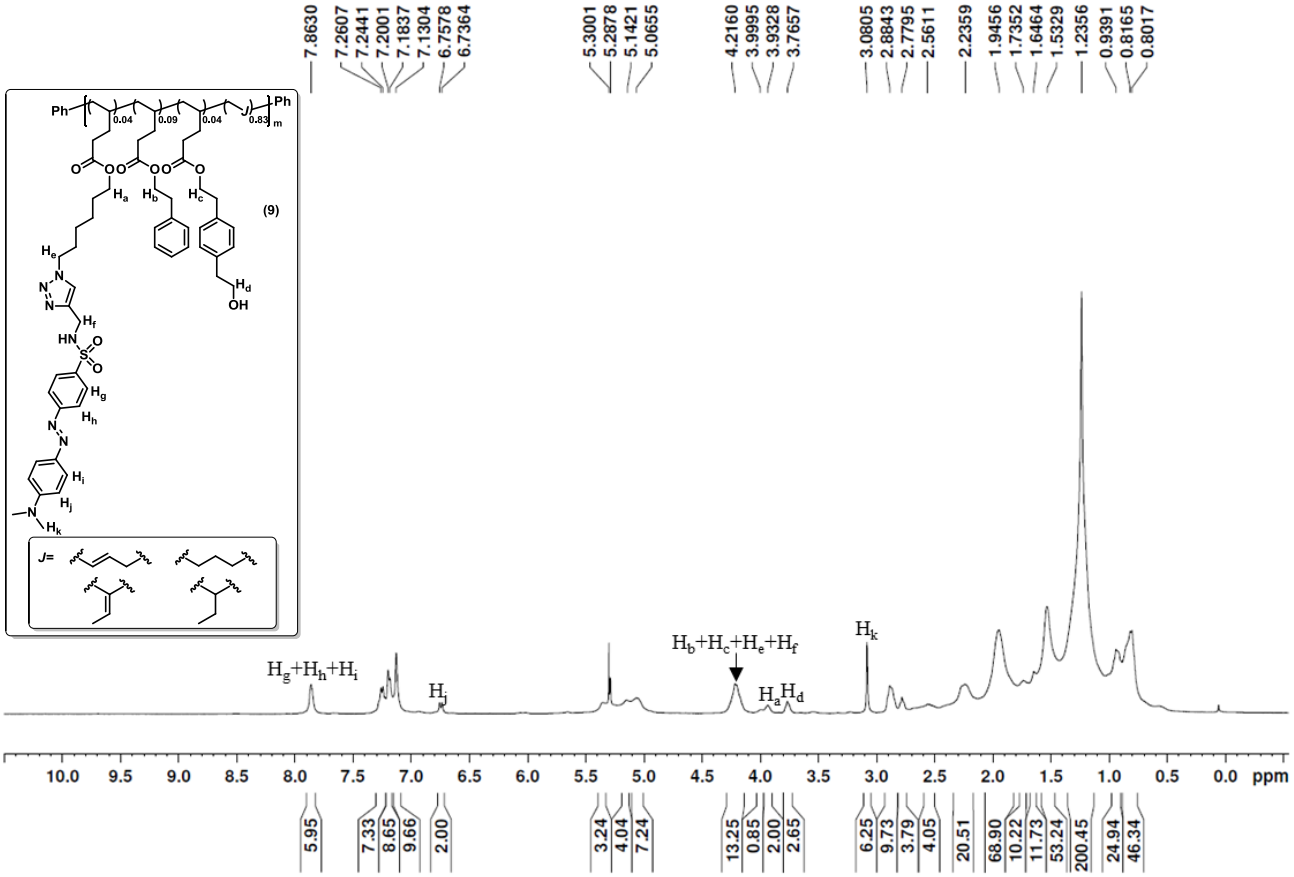
65.243
64.055
54.537
54.394
54.267
53.997
53.726
53.456
51.952
39.503
38.972
37.615
37.195
36.619
35.740
35.353
34.717
33.803
33.291
32.945
32.428
31.195
30.691
30.402
29.378
29.181
Ph
0.04
0.09
0.04
0.83
m
Ph
(7)
a
b
c
d
e
f
g
h
N_3
OH
J=
a+b+c
d+e+f+g
h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.2607
7.2441
7.2001
7.1837
7.1304
6.7578
6.7364
5.3001
5.2878
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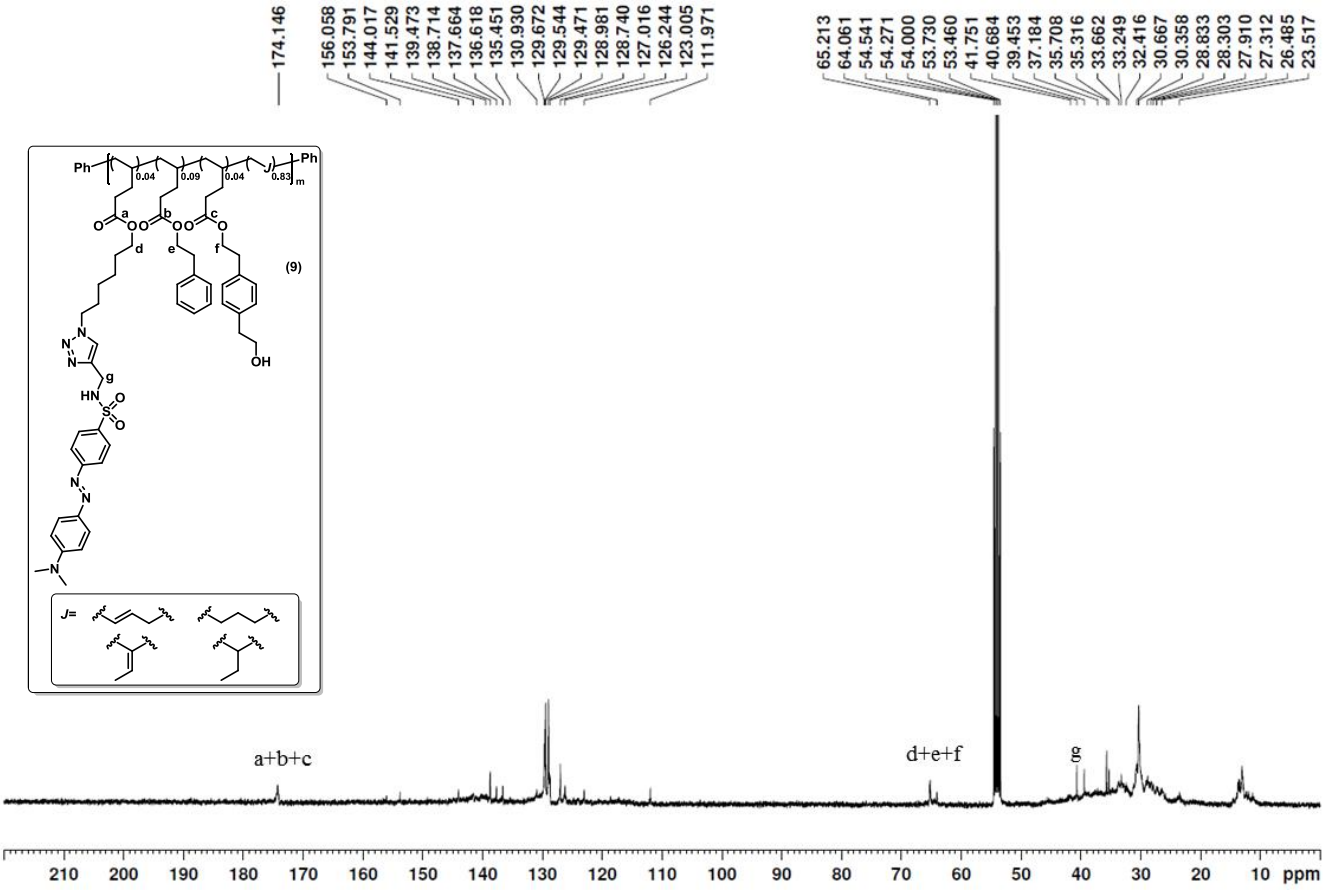
5.0655
4.2160
3.9995
3.9328
3.7657
3.0805
2.8843
2.7795
2.5611
2.2359
1.9456
1.7352
1.6464
1.5329
1.2356
0.9391
0.8165
0.8017
(9)
J=
Hg+Hh+Hi
Hj
Hb+Hc+He+Hf
Ha,Hd
Hk
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.95
7.33
8.65
9.66
2.00
3.24
4.04
7.24
13.25
0.85
2.00
2.65
6.25
9.73
3.79
4.05
20.51
68.90
10.22
11.73
53.24
200.45
24.94
46.34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144.017
141.529
139.473
138.714
137.664
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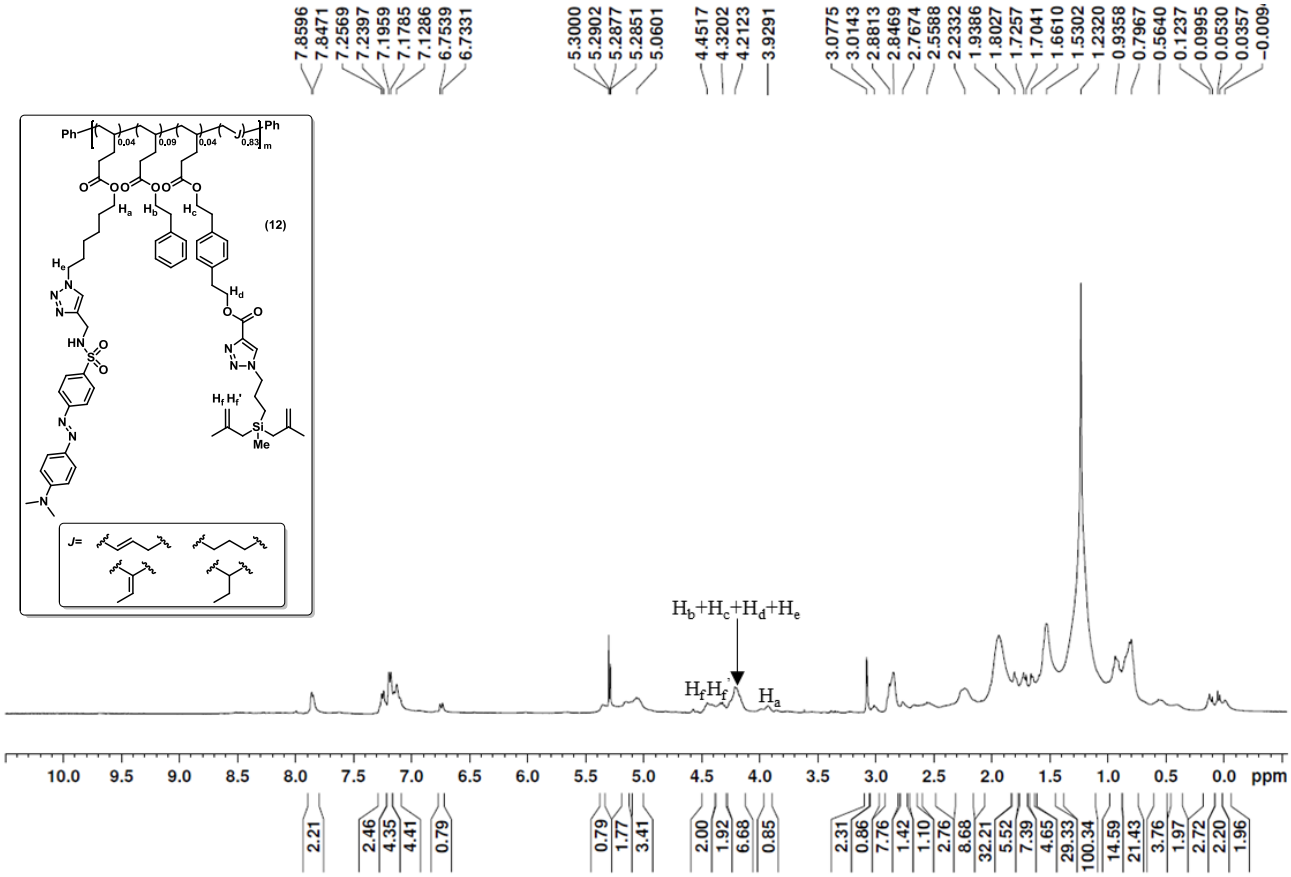
130.930
129.672
129.544
129.471
128.981
128.740
127.016
126.244
123.005
111.971
65.213
64.061
54.541
54.271
54.000
53.730
53.460
41.751
40.684
39.453
37.184
35.708
35.316
33.662
33.249
32.416
30.667
30.358
28.833
28.303
27.910
27.312
26.485
23.517
(9)
J=
a+b+c
d+e+f
g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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5.3000 5.2902 5.2877 5.2851 5.0601
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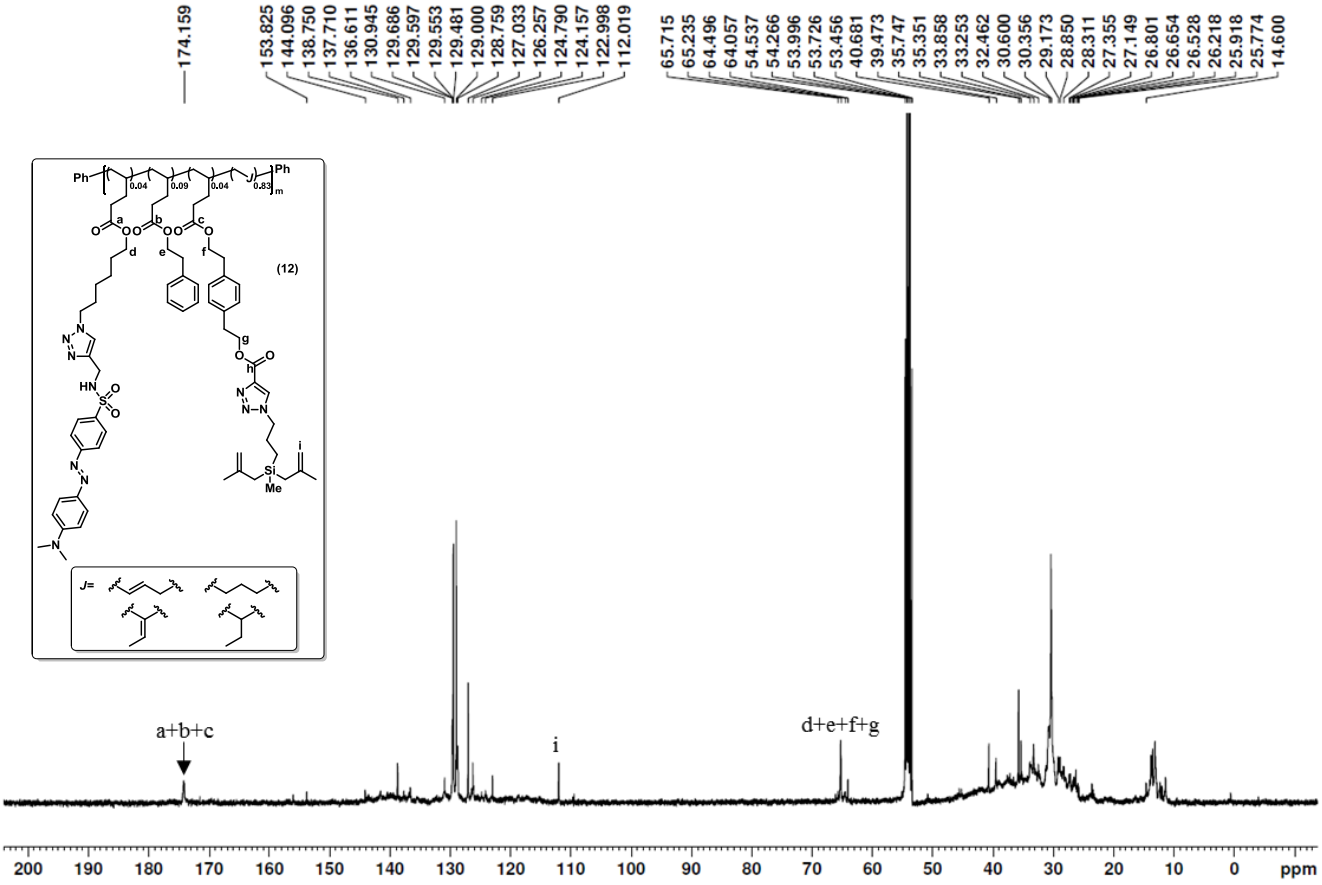
3.0775 3.0143 2.8813 2.8469 2.7674 2.5588 2.2332 1.9386 1.8027 1.7257 1.7041 1.6610 1.5302 1.2320 0.9358 0.7967 0.5640 0.1237 0.0995 0.0530 0.0357 -0.009
(12)
J=
$H_b+H_c+H_d+H_e$
H_fH_f'
H_a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.21 2.46 4.35 4.41 0.79 0.79 1.77 3.41 2.00 1.92 6.68 0.85 2.31 0.86 7.76 1.42 1.10 2.76 8.68 32.21 5.52 7.39 4.65 29.33 100.34 14.59 21.43 3.76 1.97 2.72 2.20 1.96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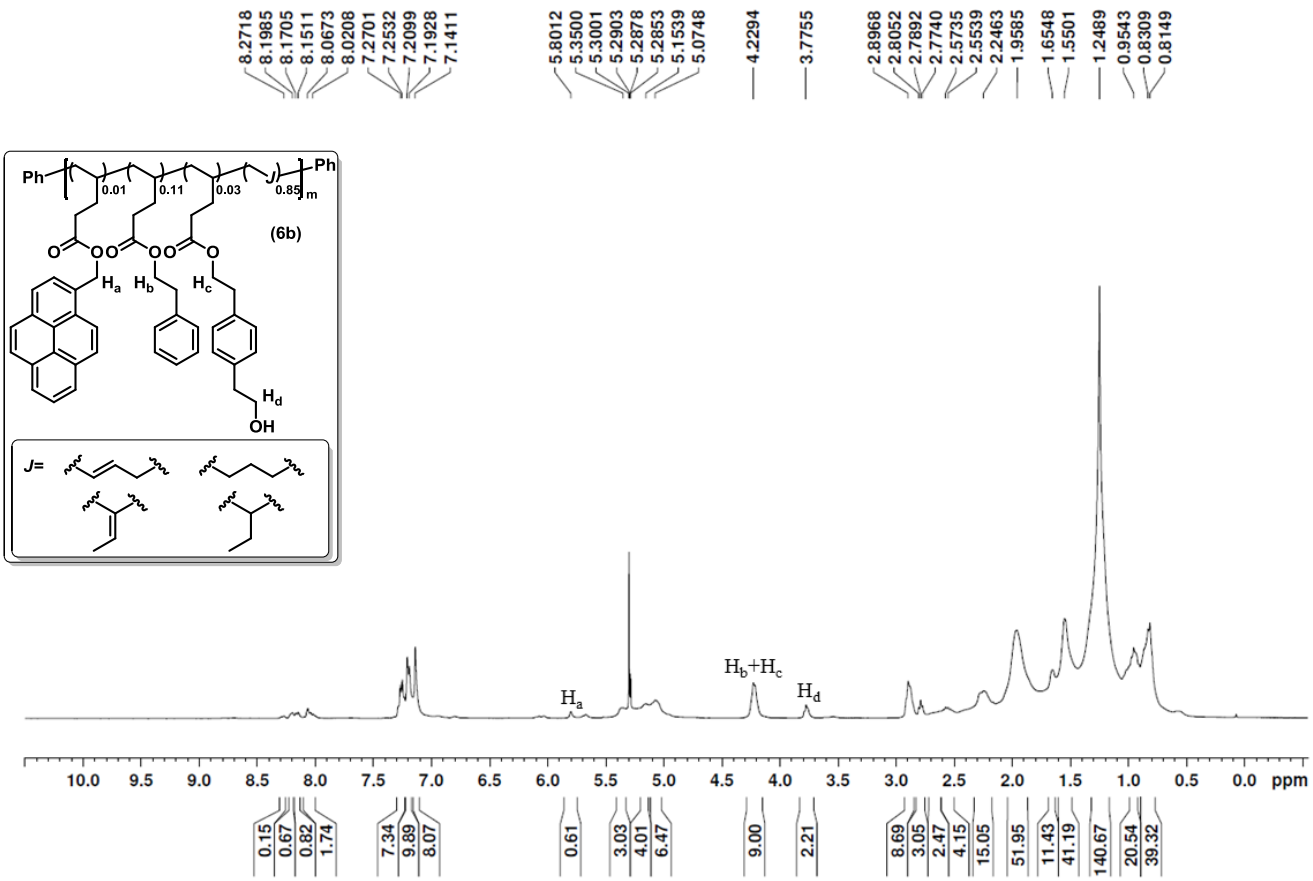
65.715 65.235 64.496 64.057 54.537 54.266 53.996 53.726 53.456 40.681 39.473 35.747 35.351 33.858 33.253 32.462 30.600 30.356 29.173 28.850 28.311 27.355 27.149 26.801 26.654 26.528 26.218 25.918 25.774 14.600
(12)
J=
a+b+c
i
d+e+f+g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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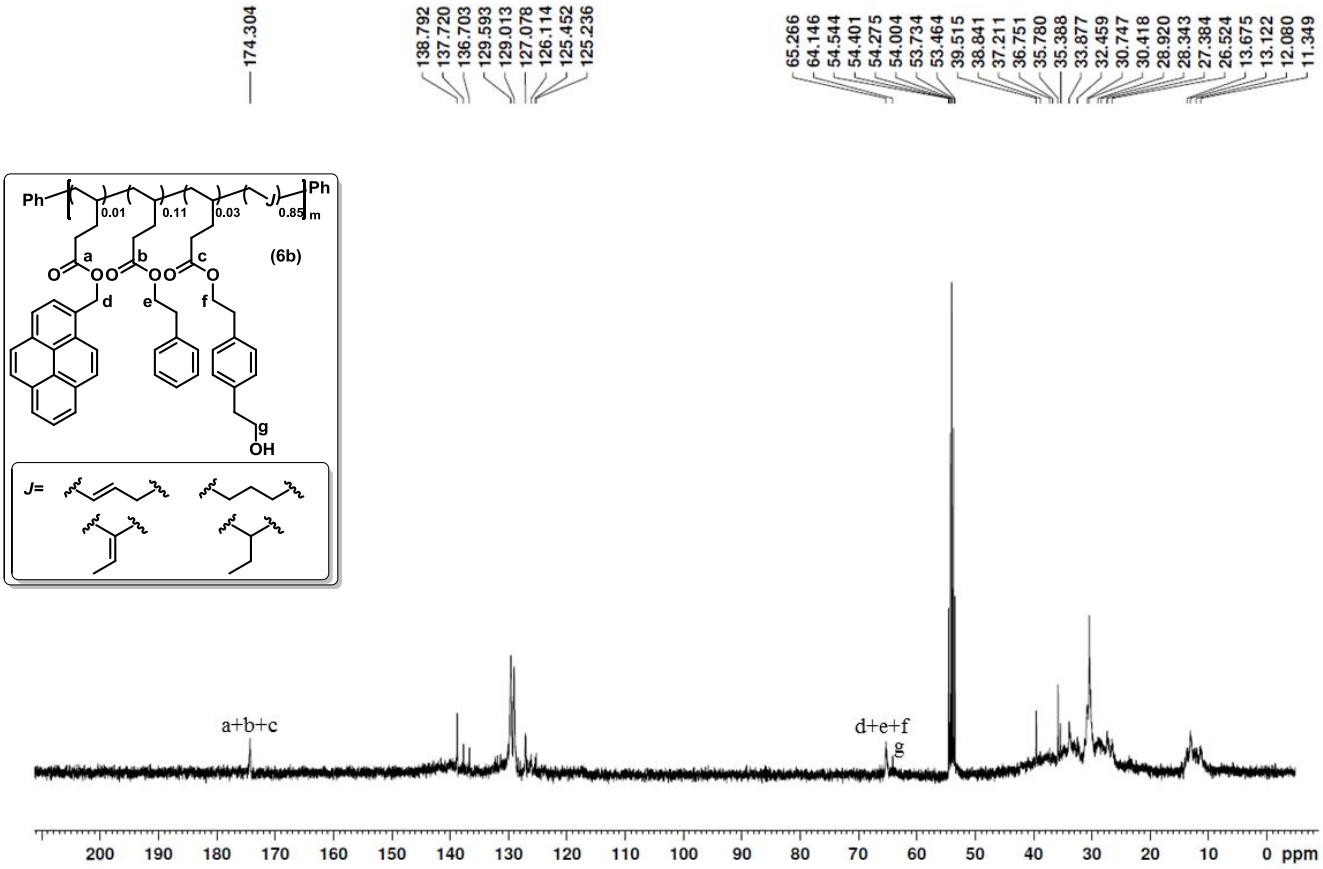
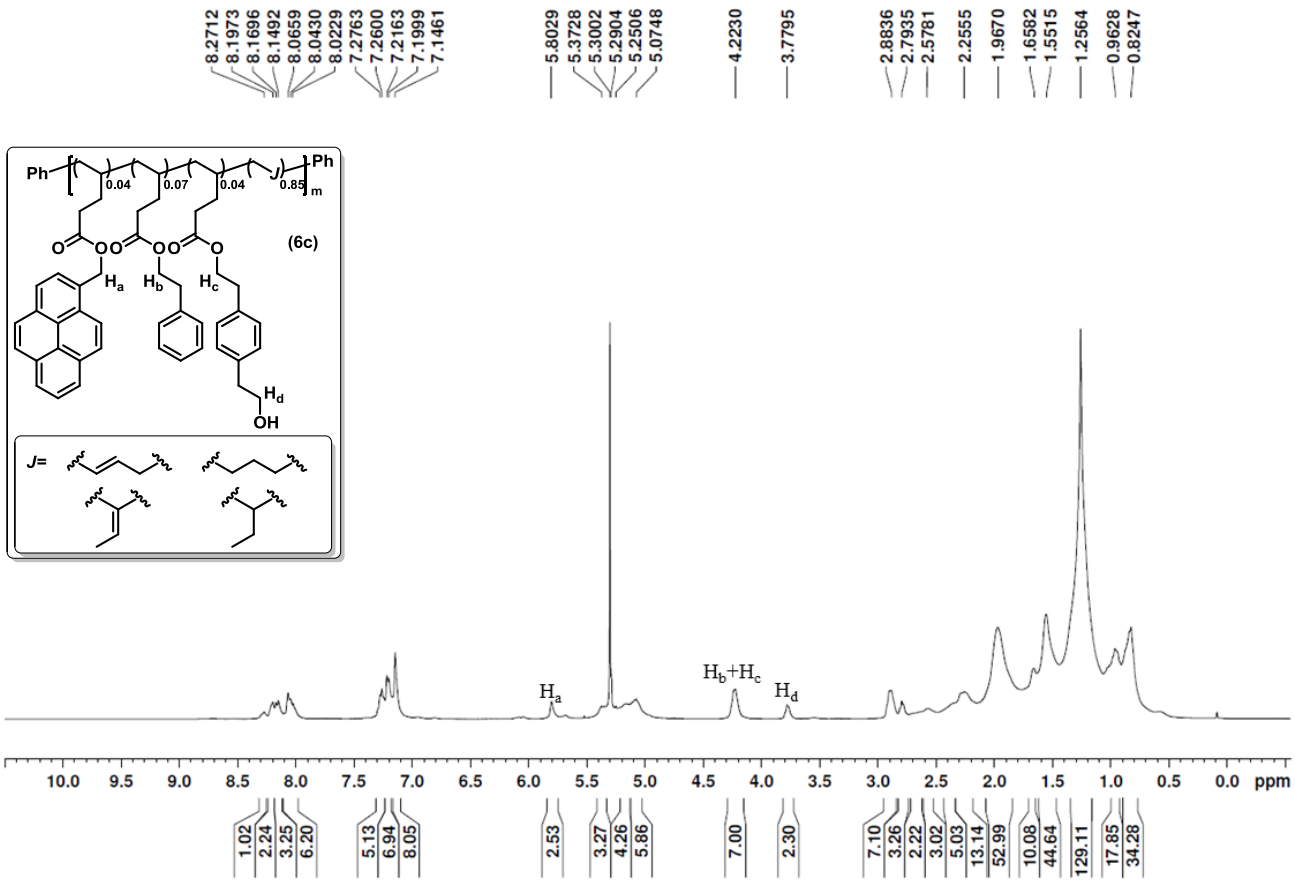
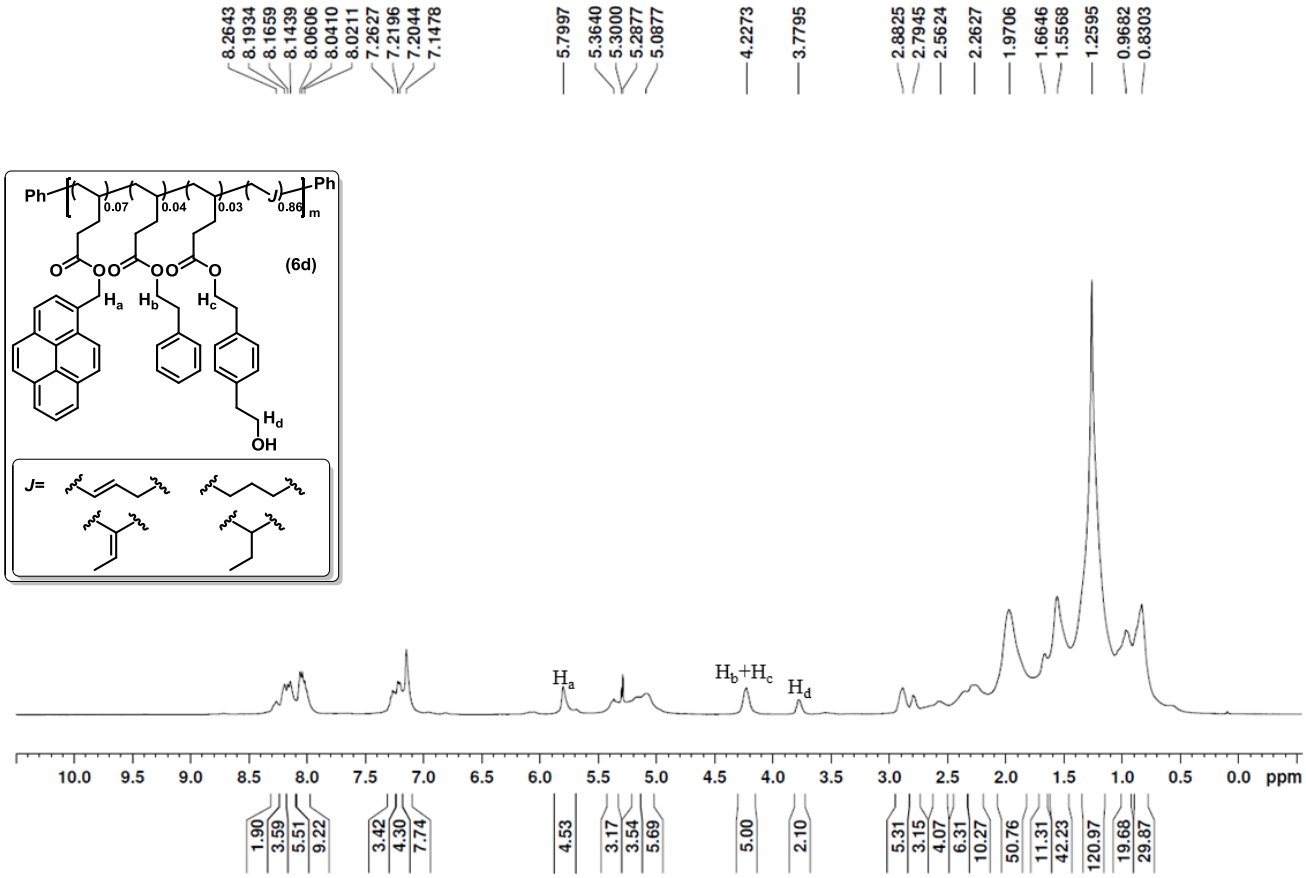
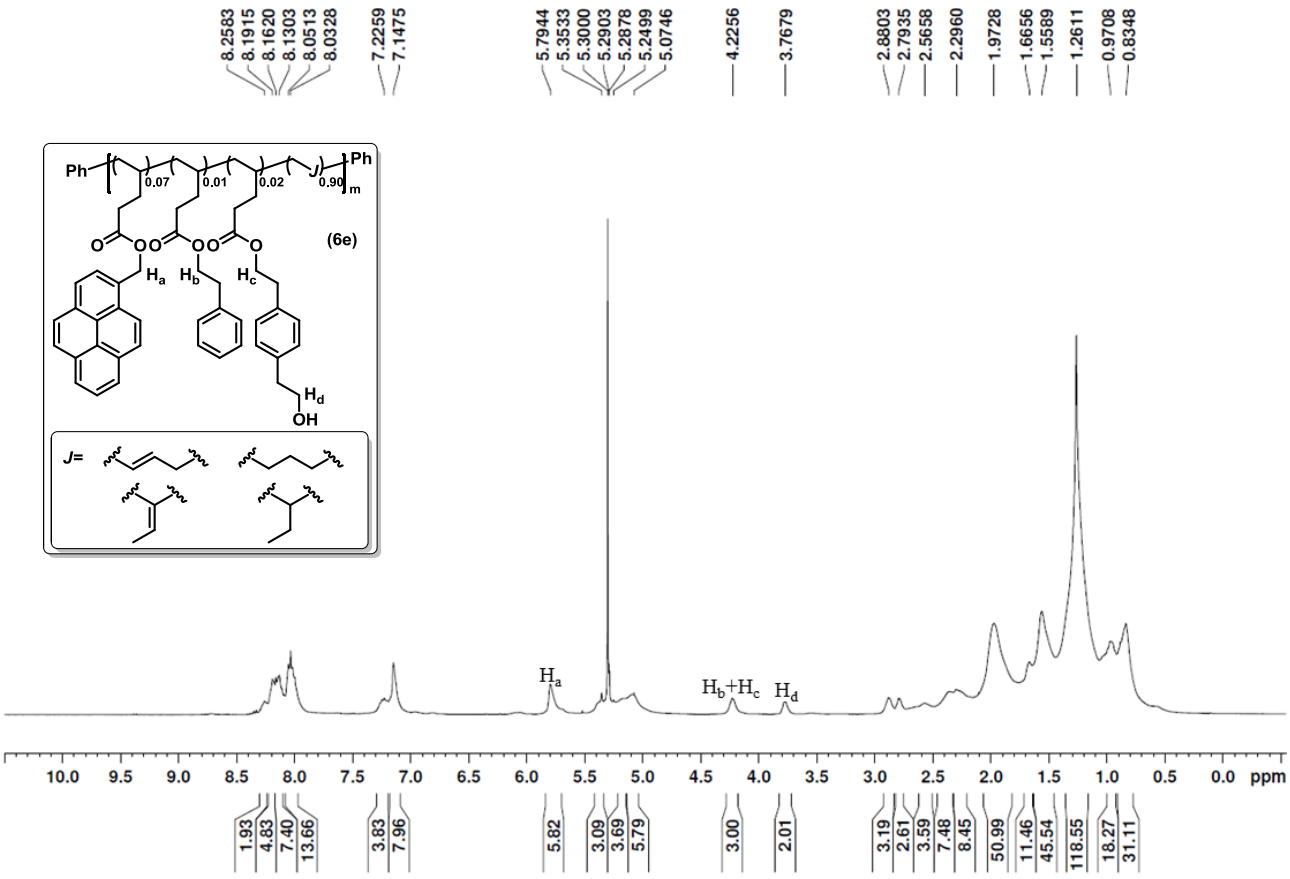
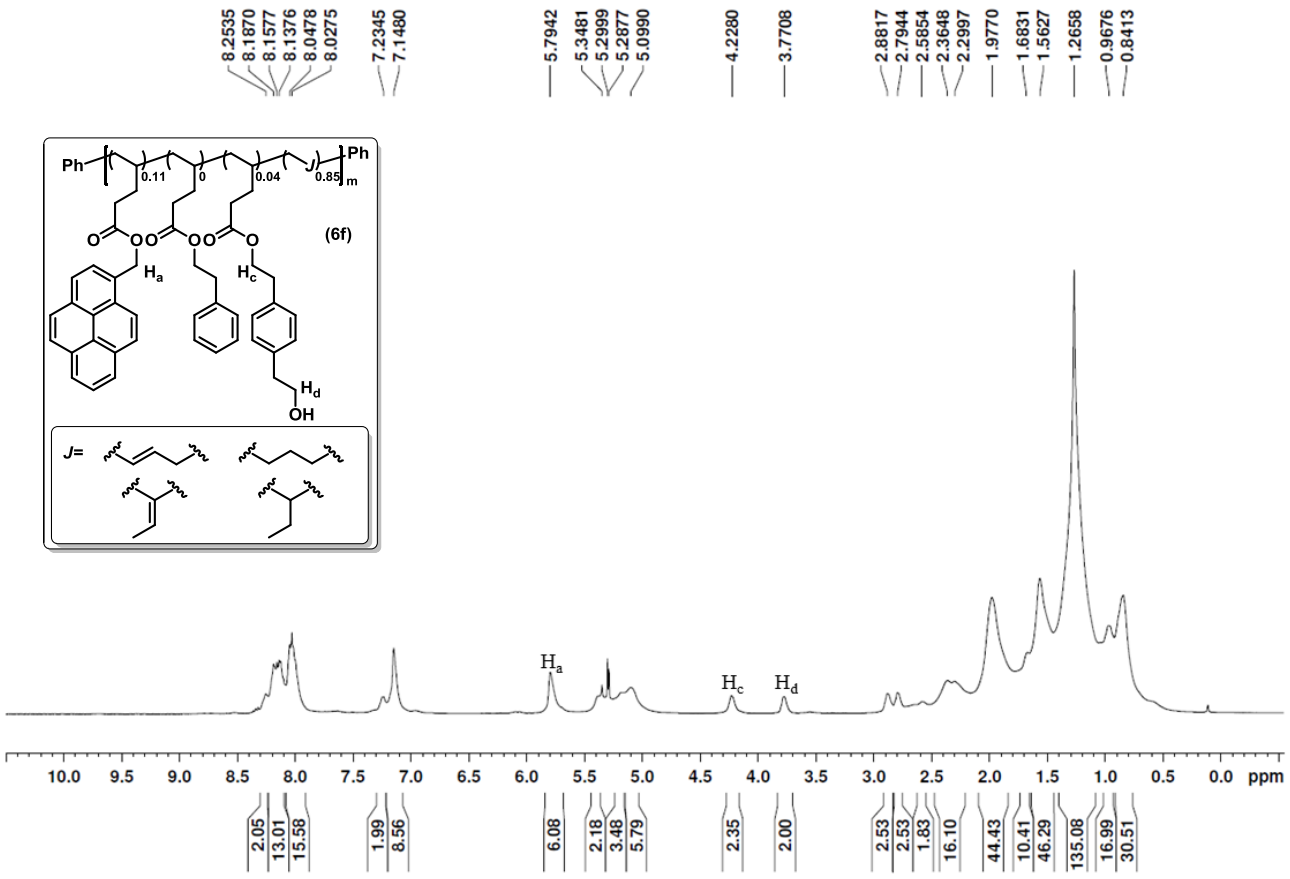
4.2294
3.7755
2.8968 2.8052 2.7892 2.7740 2.5735 2.5539 2.2463 1.9585 1.6548 1.5501 1.2489 0.9543 0.8309 0.8149
Ph
0.01
0.11
0.03
0.85
m
(6b)
Ha Hb Hc
Hd
OH
J=
Ha
Hb+Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.15 0.67 0.82 1.74
7.34 9.89 8.07
0.61
3.03 4.01 6.47
9.00
2.21
8.69 3.05 2.47 4.15 15.05 51.95 11.43 41.19 140.67 20.54 39.32

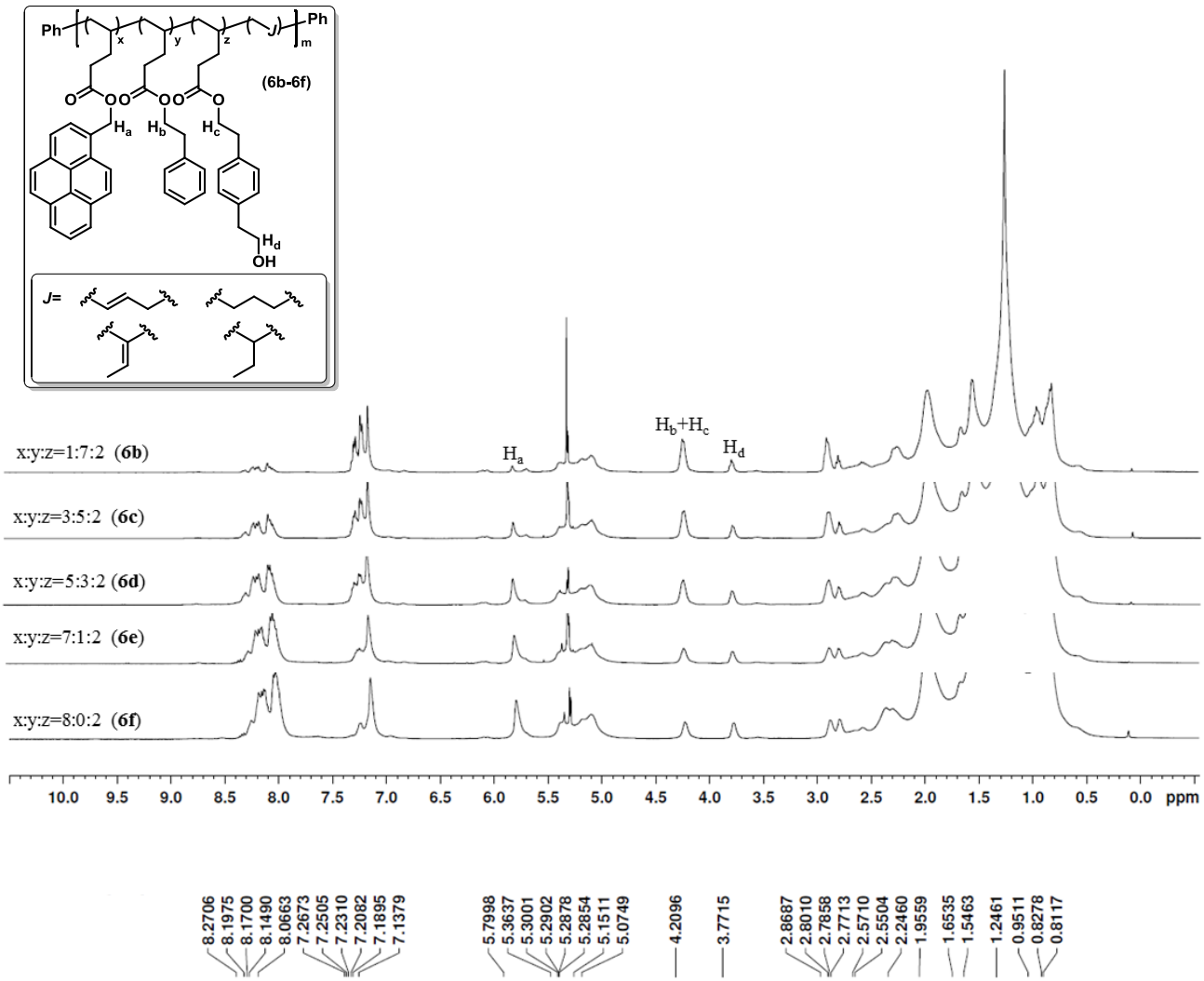

174.304
138.792 137.720 136.703 129.593 129.013 127.078 126.114 125.452 125.236
65.266 64.146 54.544 54.401 54.275 54.004 53.734 53.464 39.515 38.841 37.211 36.751 35.780 35.388 33.877 32.459 30.747 30.418 28.920 28.343 27.384 26.524 13.675 13.122 12.080 11.349
Ph
0.01
0.11
0.03
0.85
m
(6b)
a b c
d e f
g
OH
J=
a+b+c
d+e+f
g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

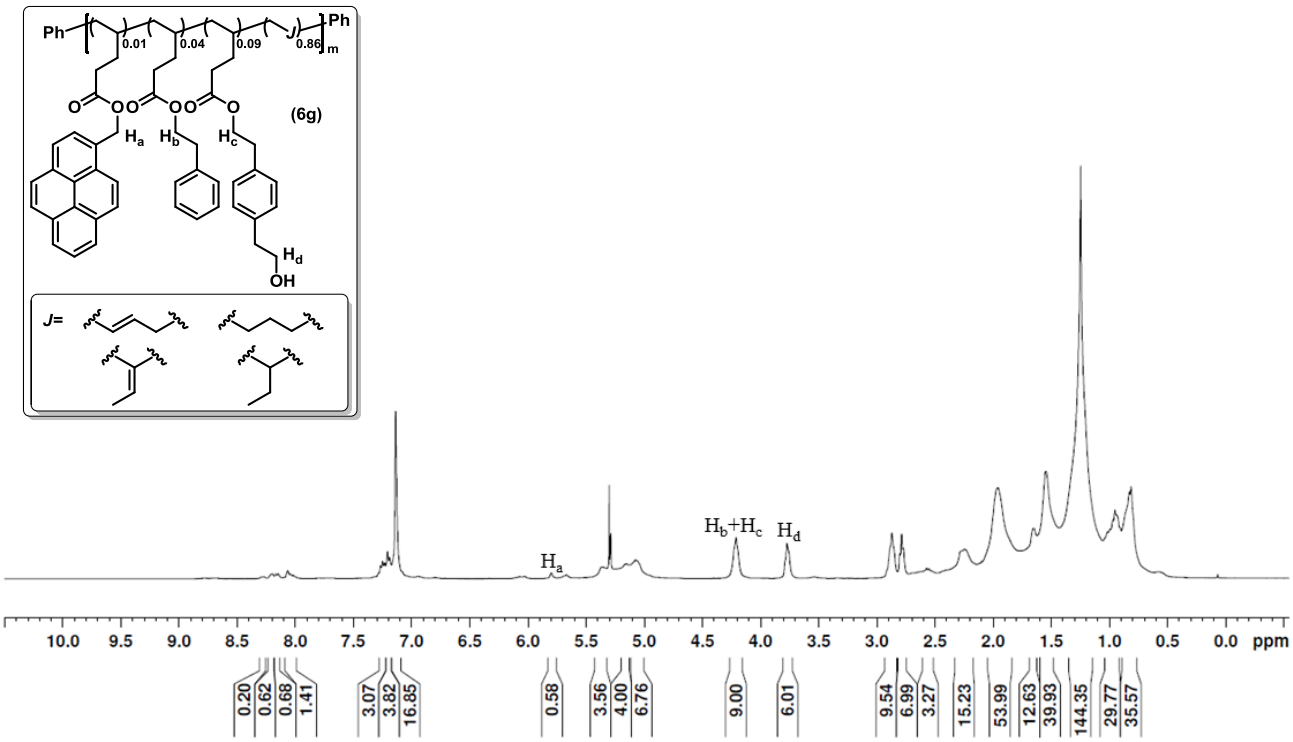

8.2712 8.1973 8.1696 8.1492 8.0659 8.0430 8.0229 7.2763 7.2600 7.2163 7.1999 7.1461
5.8029 5.3728 5.3002 5.2904 5.2506 5.0748
4.2230
3.7795
2.8836 2.7935 2.5781
2.2555
1.9670
1.6582 1.5515
1.2564
0.9628 0.8247
Ph
0.04
0.07
0.04
0.85
m
Ph
(6c)
Ha
Hb
Hc
Hd
OH
J=
Ha
Hb+Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02 2.24 3.25 6.20
5.13 6.94 8.05
2.53
3.27 4.26 5.86
7.00
2.30
7.10 3.26 2.22 3.02 5.03 13.14 52.99 10.08 44.64 129.11 17.85 34.28

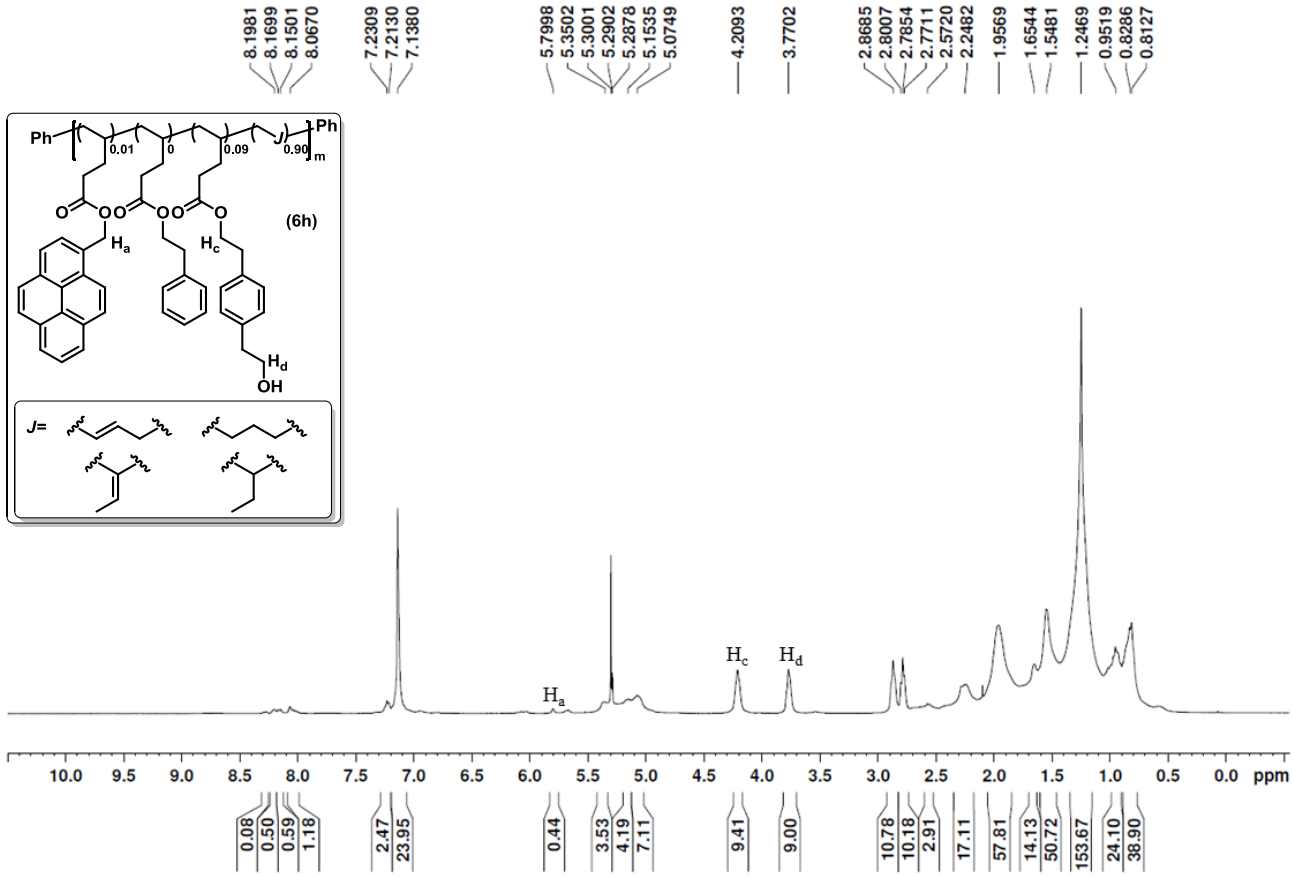

8.2643 8.1934 8.1659 8.1439 8.0606 8.0410 8.0211 7.2627 7.2196 7.2044 7.1478
5.7997 5.3640 5.3000 5.2877 5.0877
4.2273
3.7795
2.8825 2.7945 2.5624
2.2627
1.9706
1.6646 1.5568
1.2595
0.9682 0.8303
Ph
0.07
0.04
0.03
0.86
m
Ph
(6d)
Ha
Hb
Hc
Hd
OH
J=
Ha
Hb+Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.90 3.59 5.51 9.22
3.42 4.30 7.74
4.53
3.17 3.54 5.69
5.00
2.10
5.31 3.15 4.07 6.31 10.27 50.76 11.31 42.23 120.97 19.68 29.87

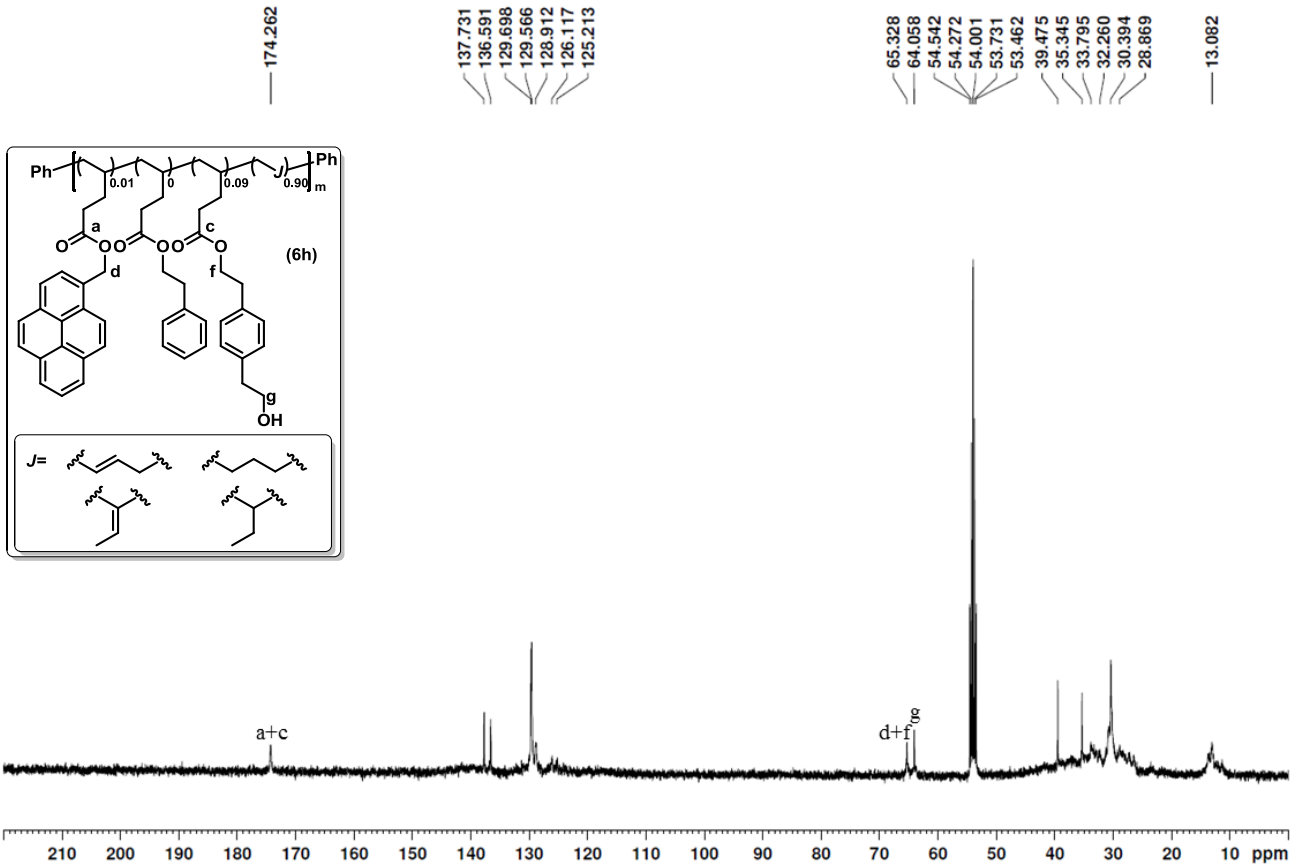

8.2583 8.1915 8.1620 8.1303 8.0513 8.0328 7.2259 7.1475 5.7944 5.3533 5.3000 5.2903 5.2878 5.2499 5.0746 4.2256 3.7679 2.8803 2.7935 2.5658 2.2960 1.9728 1.6656 1.5589 1.2611 0.9708 0.8348
Ph
0.07
0.01
0.02
0.90
m
Ph
(6e)
Ha
Hb
Hc
Hd
OH
J=
Ha
Hb+Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.93 4.83 7.40 13.66 3.83 7.96 5.82 3.09 3.69 5.79 3.00 2.01 3.19 2.61 3.59 7.48 8.45 50.99 11.46 45.54 118.55 18.27 31.11

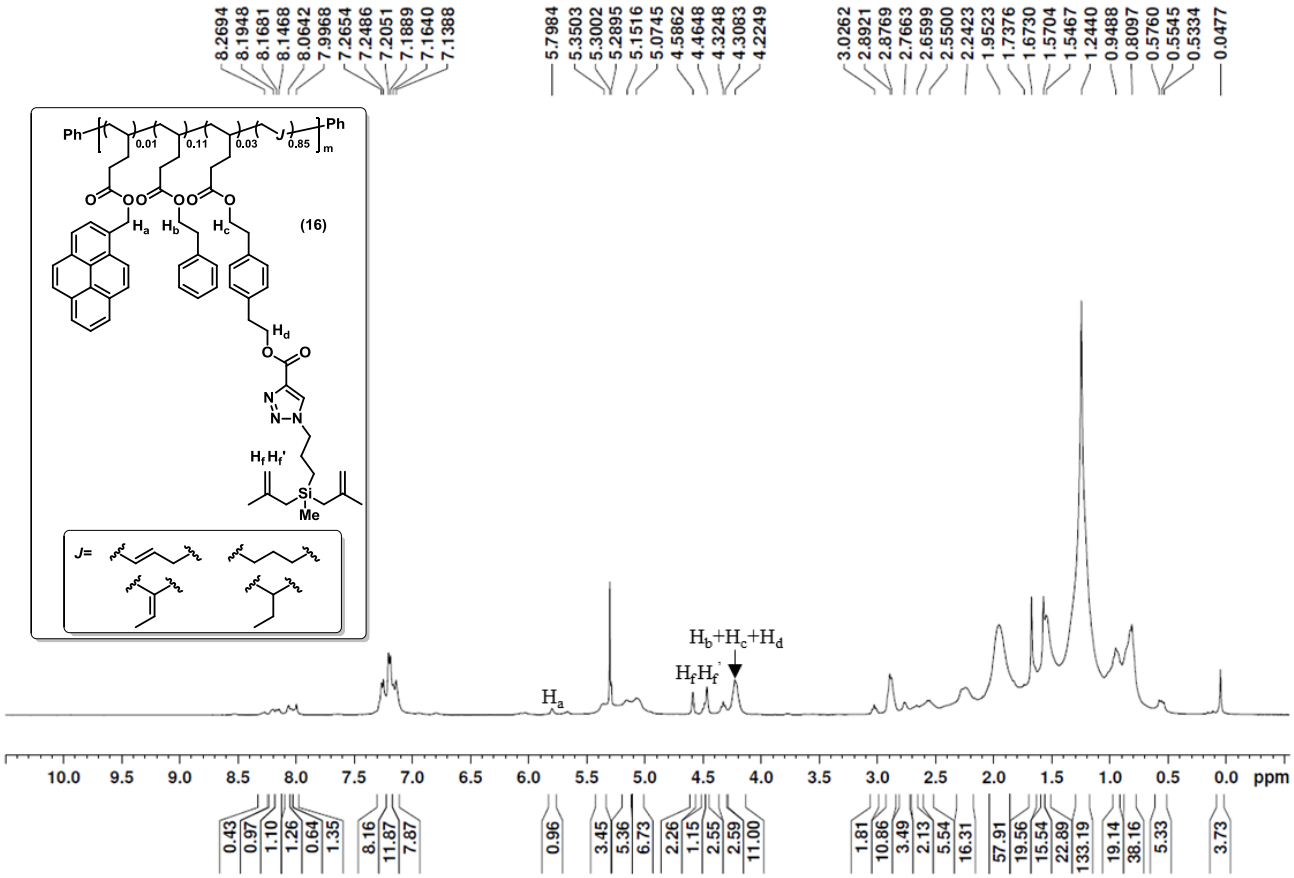

8.2535 8.1870 8.1577 8.1376 8.0478 8.0275 7.2345 7.1480 5.7942 5.3481 5.2999 5.2877 5.0990 4.2280 3.7708 2.8817 2.7944 2.5854 2.3648 2.2997 1.9770 1.6831 1.5627 1.2658 0.9676 0.8413
Ph
0.11
0
0.04
0.85
m
Ph
(6f)
Ha
Hc
Hd
OH
J=
Ha
Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05 13.01 15.58 1.99 8.56 6.08 2.18 3.48 5.79 2.35 2.00 2.53 2.53 1.83 16.10 44.43 10.41 46.29 135.08 16.99 30.51

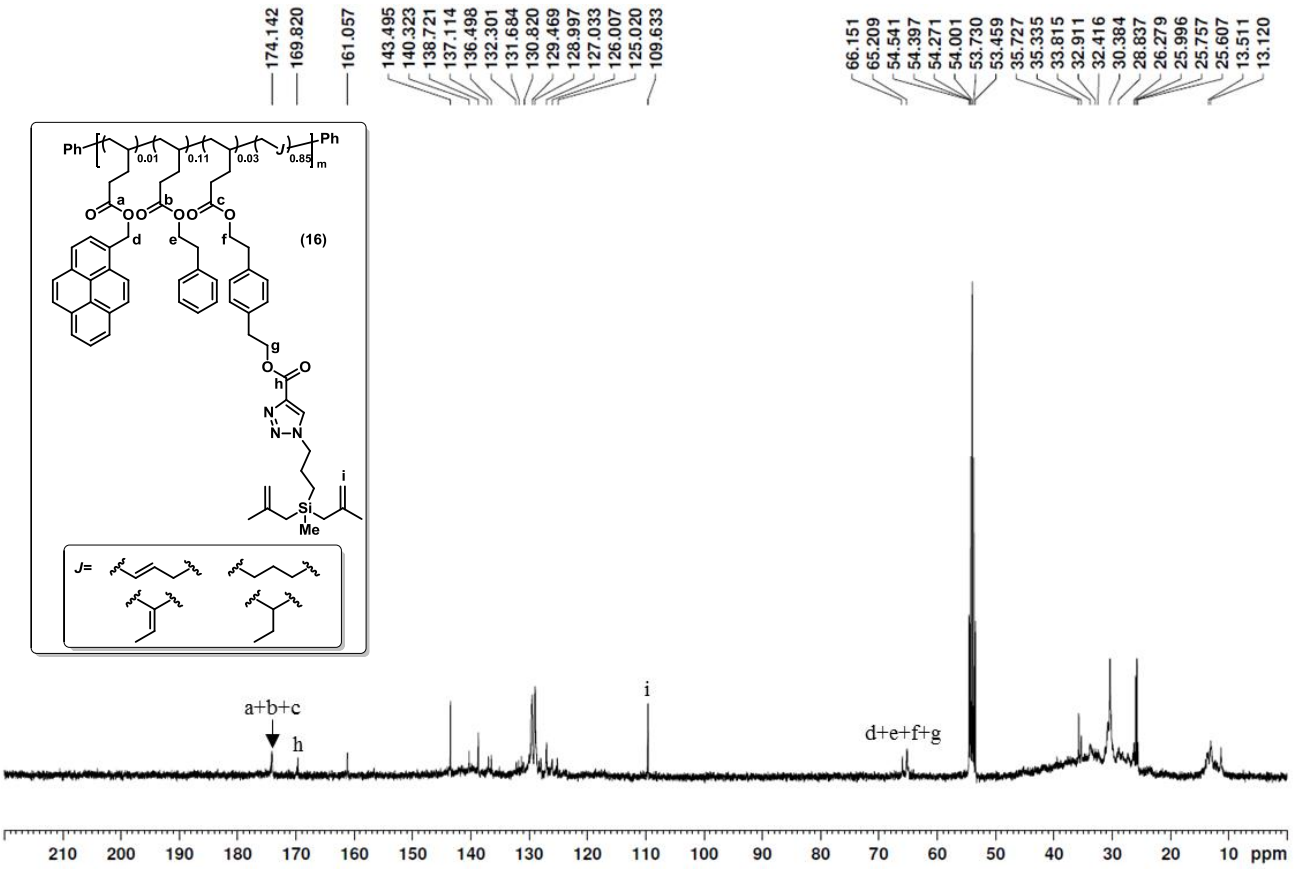

(6b-6f)
J=
x:y:z=1:7:2 (6b)
x:y:z=3:5:2 (6c)
x:y:z=5:3:2 (6d)
x:y:z=7:1:2 (6e)
x:y:z=8:0:2 (6f)
Ha
Hb+Hc
Hd
ppm
8.2706 8.1975 8.1700 8.1490 8.0663 7.2673 7.2505 7.2310 7.2082 7.1895 7.1379
5.7998 5.3637 5.3001 5.2902 5.2878 5.2854 5.1511 5.0749
4.2096
3.7715
2.8687 2.8010 2.7858 2.7713 2.5710 2.5504 2.2460 1.9559 1.6535 1.5463 1.2461 0.9511 0.8278 0.8117


(6g)
J=
Ha
Hb+Hc
Hd
ppm
0.20 0.62 0.68 1.41 3.07 3.82 16.85 0.58 3.56 4.00 6.76 9.00 6.01 9.54 6.99 3.27 15.23 53.99 12.63 39.93 144.35 29.77 35.57

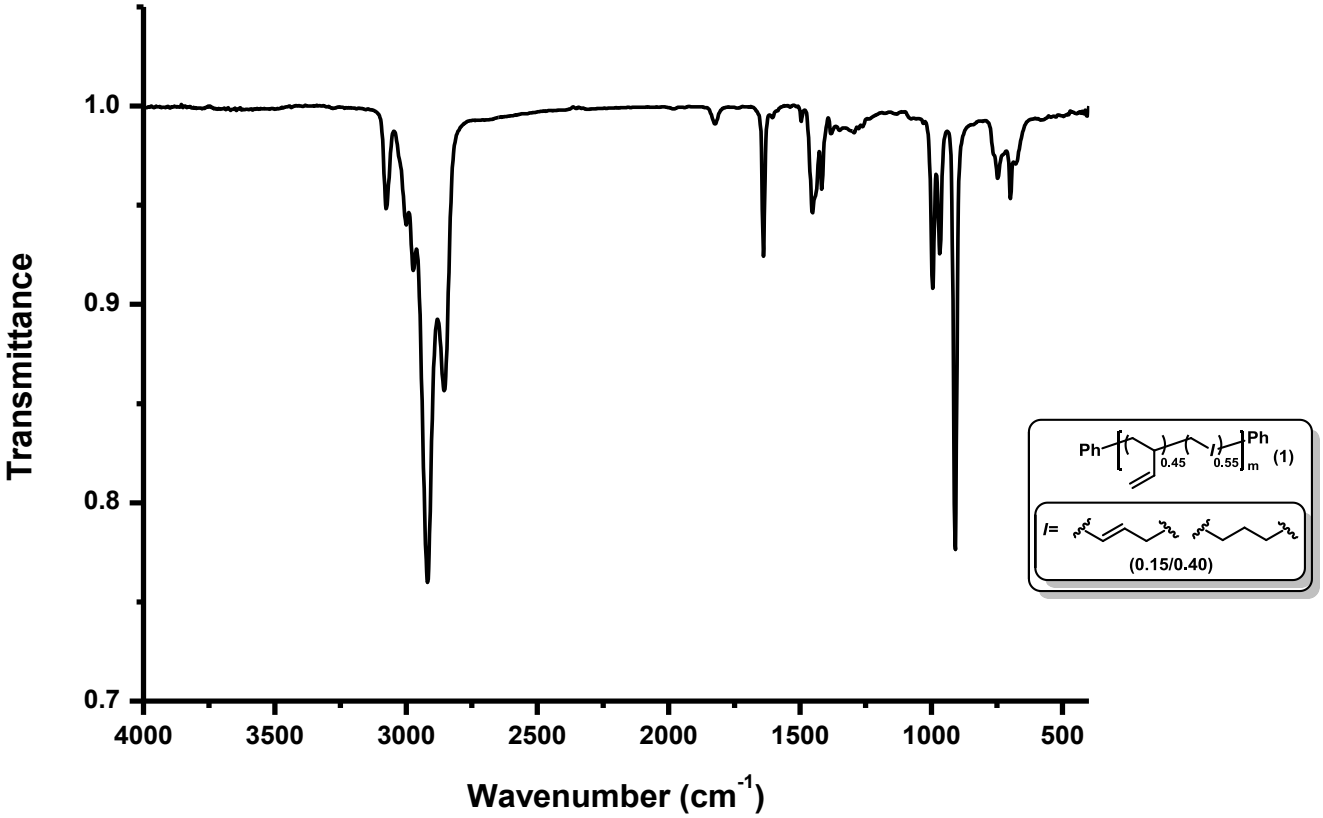

8.1981
8.1699
8.1501
8.0670
7.2309
7.2130
7.1380
5.7998
5.3502
5.3001
5.2902
5.2878
5.1535
5.0749
4.2093
3.7702
2.8685
2.8007
2.7854
2.7711
2.5720
2.2482
1.9569
1.6544
1.5481
1.2469
0.9519
0.8286
0.8127
Ph
0.01
0
0.09
0.90
m
(6h)
Ha
Hc
Hd
OH
J=
Ha
Hc
Hd
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.08
0.50
0.59
1.18
2.47
23.95
0.44
3.53
4.19
7.11
9.41
9.00
10.78
10.18
2.91
17.11
57.81
14.13
50.72
153.67
24.10
38.90

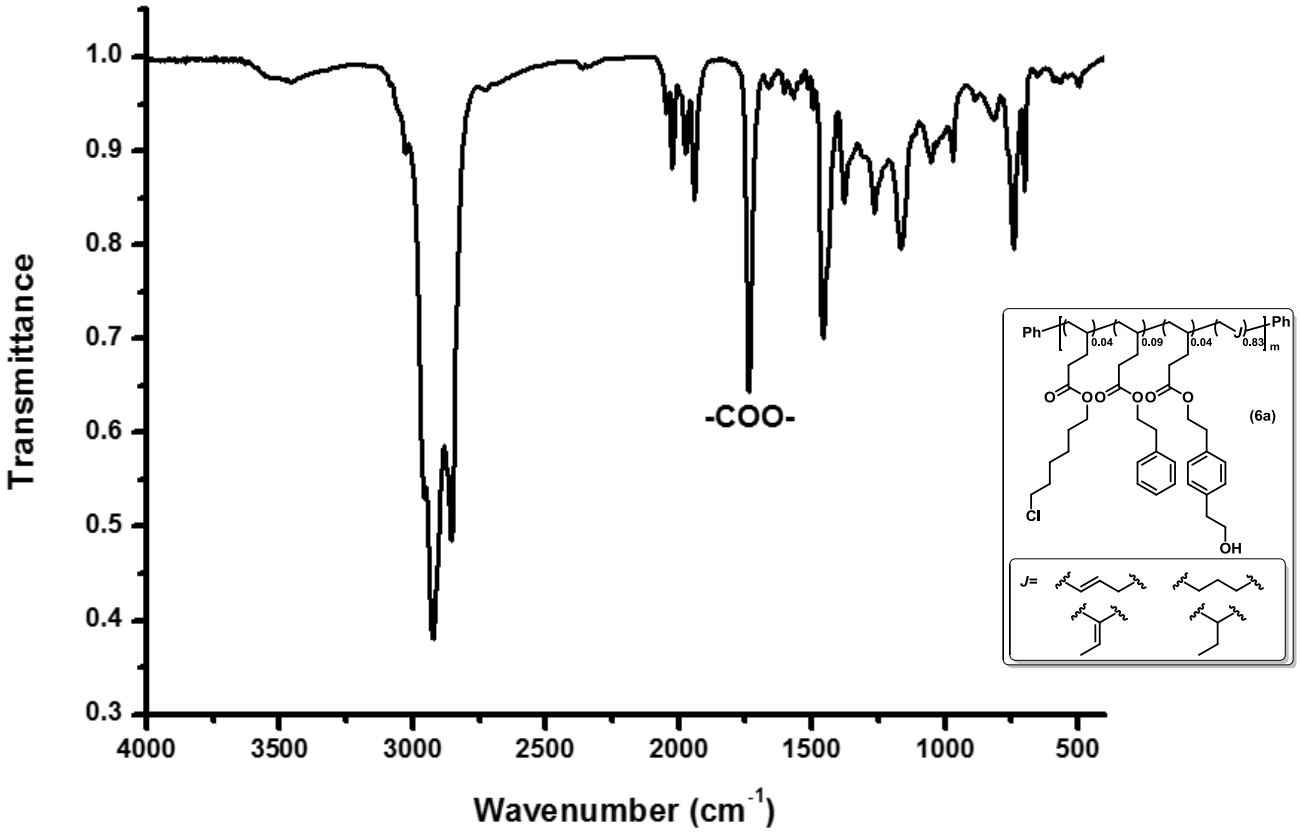

174.262
137.731
136.591
129.698
129.566
128.912
126.117
125.213
65.328
64.058
54.542
54.272
54.001
53.731
53.462
39.475
35.345
33.795
32.260
30.394
28.869
13.082
Ph
0.01
0
0.09
0.90
m
a
c
d
f
g
(6h)
OH
J=
a+c
d+f
g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

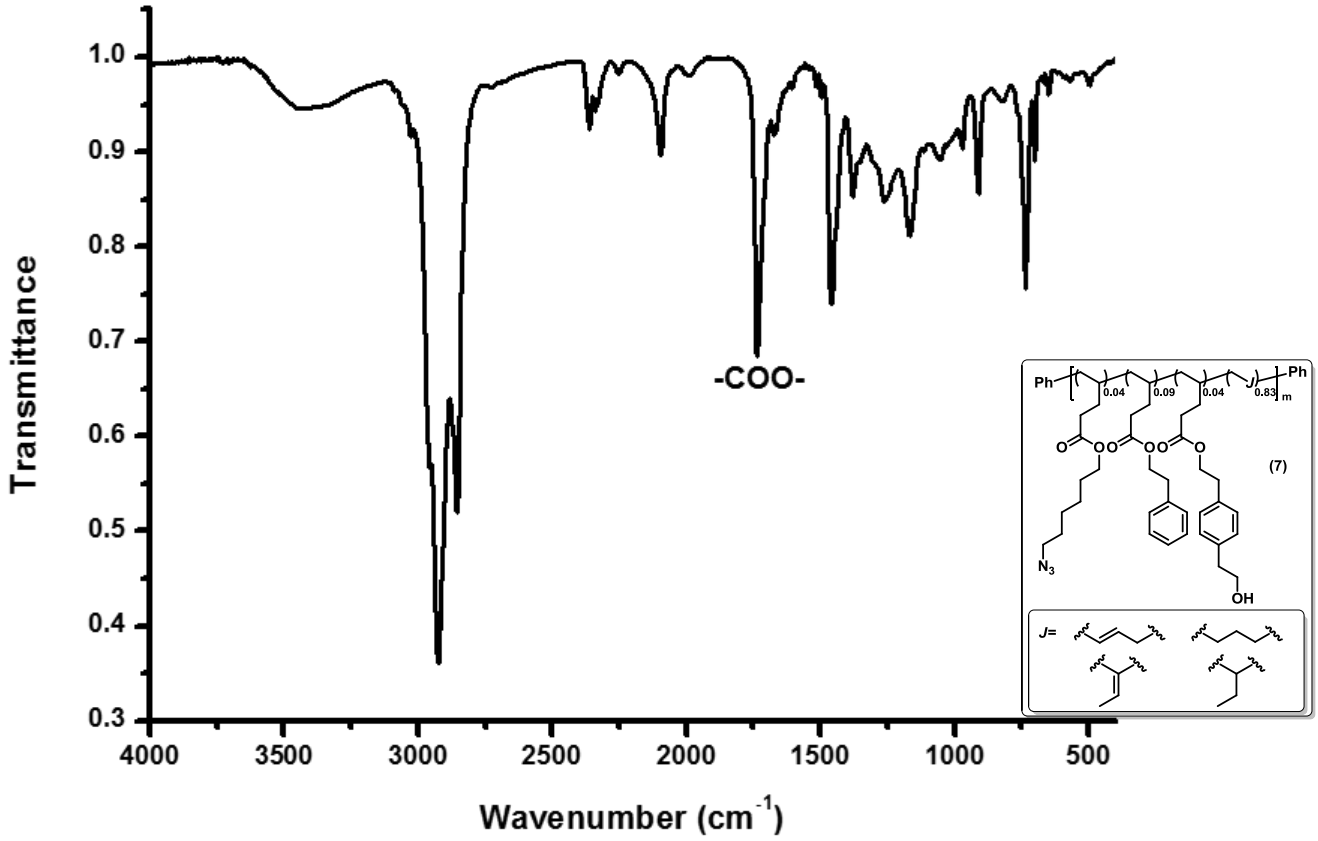

8.2694 8.1948 8.1681 8.1468 8.0642 7.9968 7.2654 7.2486 7.2051 7.1889 7.1640 7.1388
5.7984 5.3503 5.3002 5.2895 5.1516 5.0745 4.5862 4.4648 4.3248 4.3083 4.2249
3.0262 2.8921 2.8769 2.7663 2.6599 2.5500 2.2423 1.9523 1.7376 1.6730 1.5704 1.5467 1.2440 0.9488 0.8097 0.5760 0.5545 0.5334 0.0477
(16)
J=
Ha
Hb+Hc+Hd
HfHf'
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.43 0.97 1.10 1.26 0.64 1.35 8.16 11.87 7.87 0.96 3.45 5.36 6.73 2.26 1.15 2.55 2.59 11.00 1.81 10.86 3.49 2.13 5.54 16.31 57.91 19.56 15.54 22.89 133.19 19.14 38.16 5.33 3.73

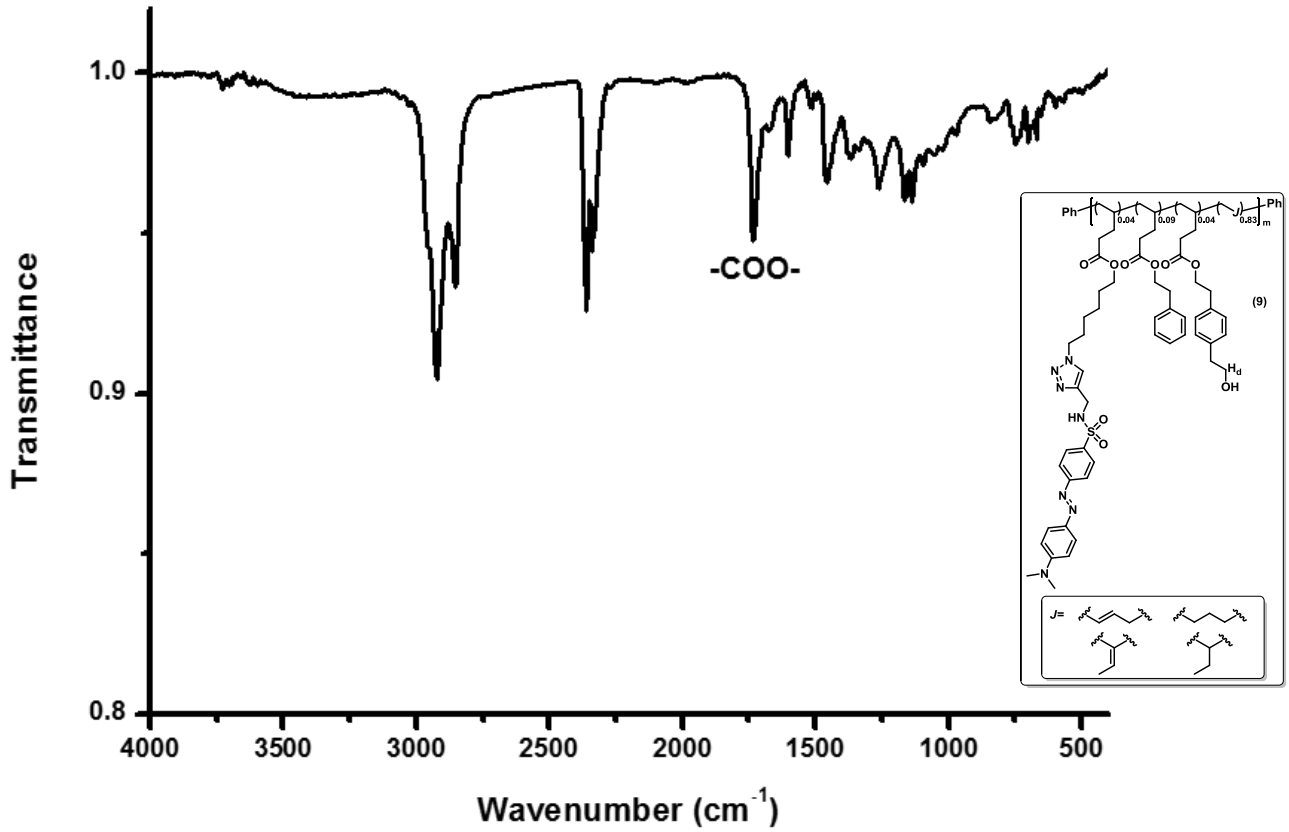

174.142 169.820 161.057 143.495 140.323 138.721 137.114 136.498 132.301 131.684 130.820 129.469 128.997 127.033 126.007 125.020 109.633
66.151 65.209 54.541 54.397 54.271 54.001 53.730 53.459 35.727 35.335 33.815 32.911 32.416 30.384 28.837 26.279 25.996 25.757 25.607 13.511 13.120
(16)
J=
a+b+c
h
i
d+e+f+g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

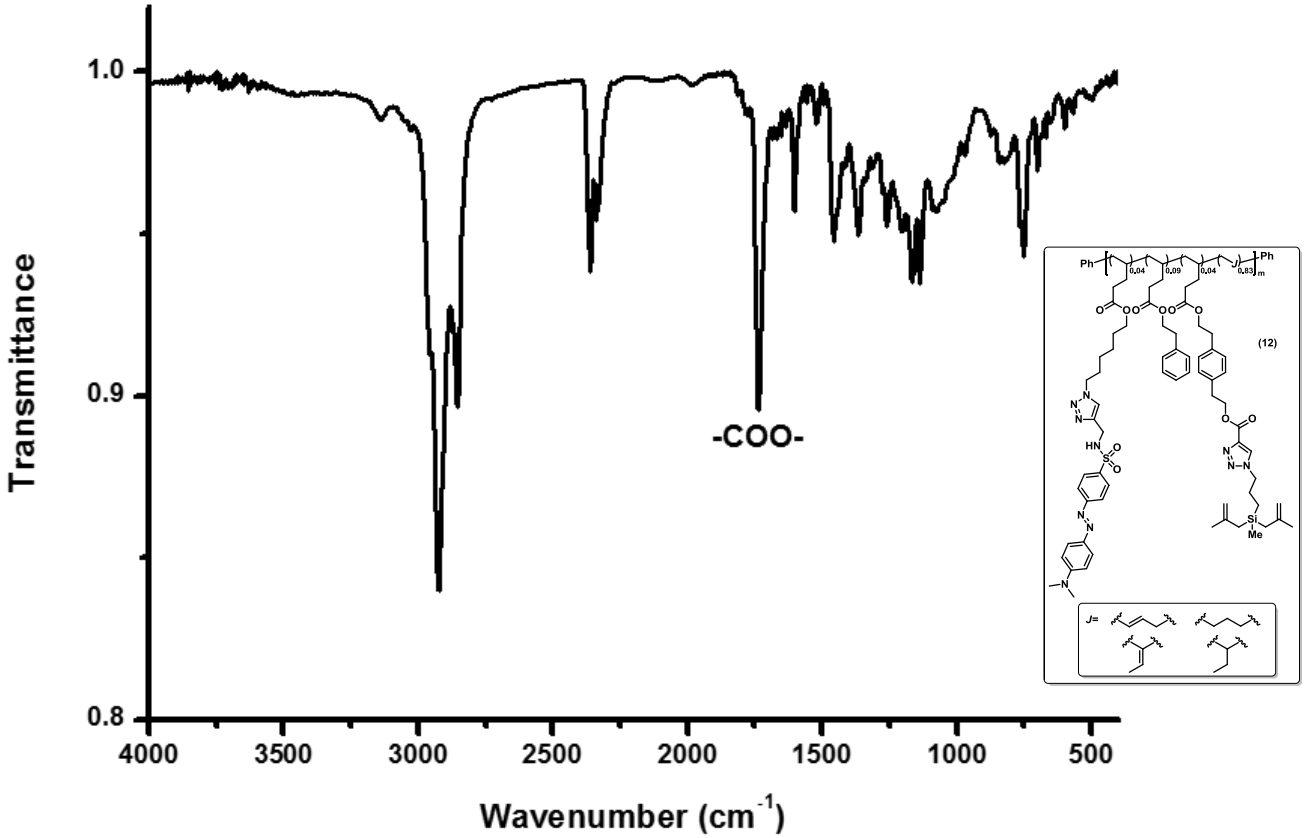
5. IR SPECTRA

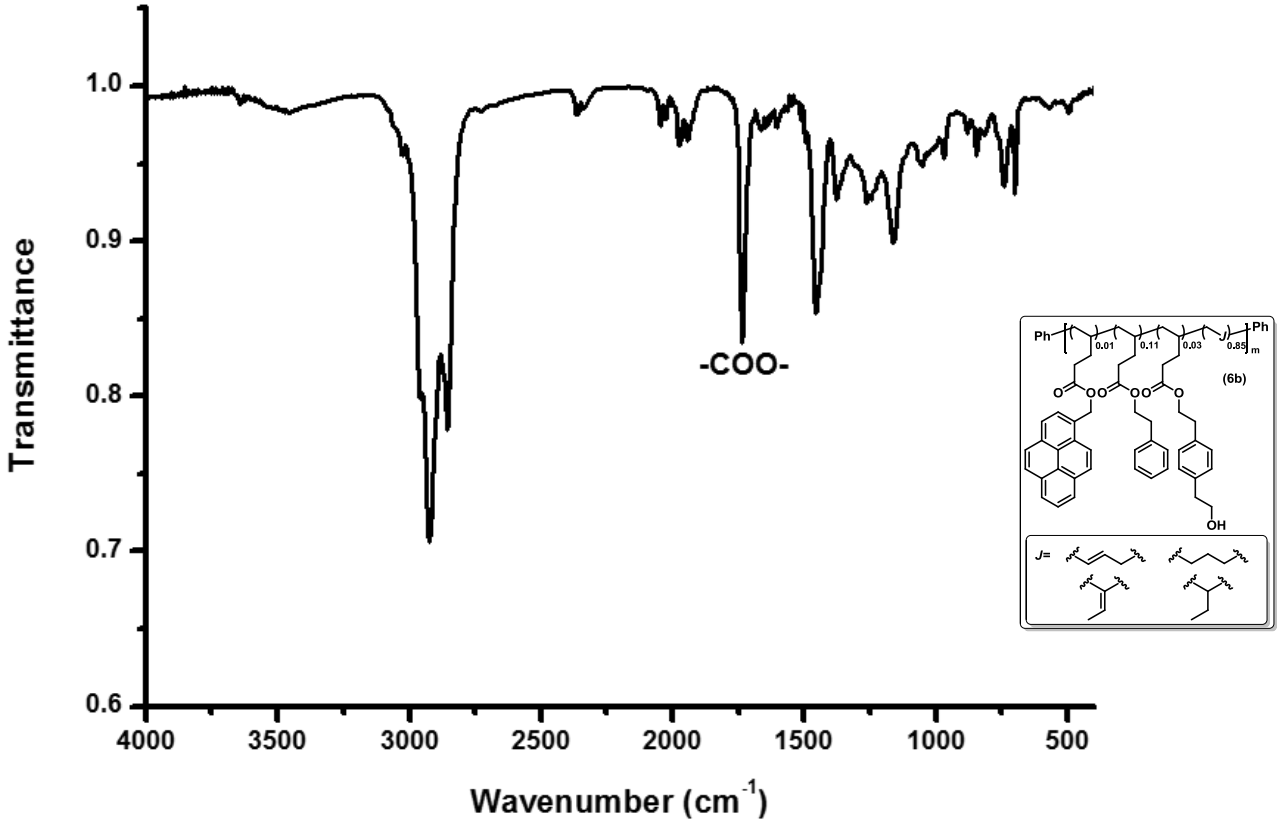

Transmittance
1.0
0.9
0.8
0.7
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
Ph
0.45
0.55
m
Ph
(1)
l=
(0.15/0.40)

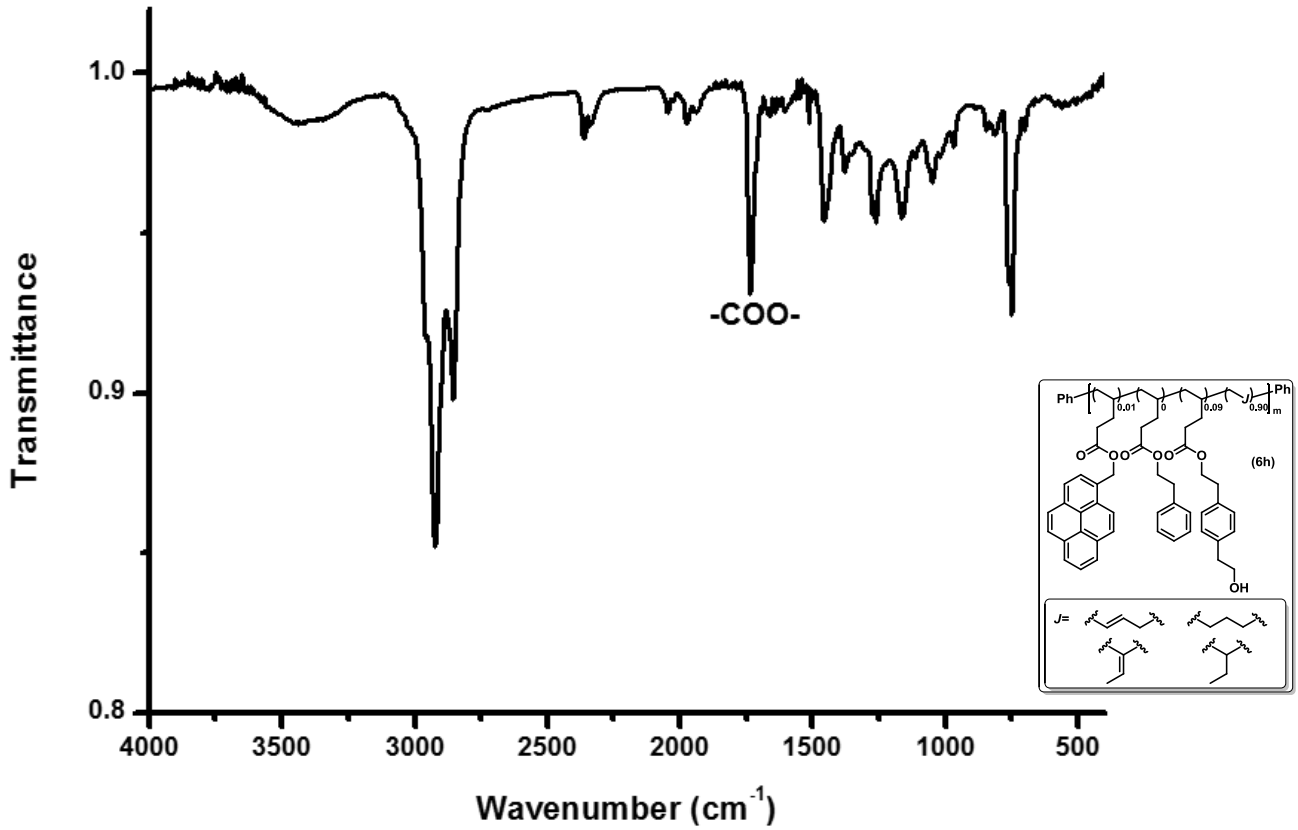

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
-COO-
Ph
0.04
0.09
0.04
0.83
m
Ph
(6a)
Cl
OH
J=

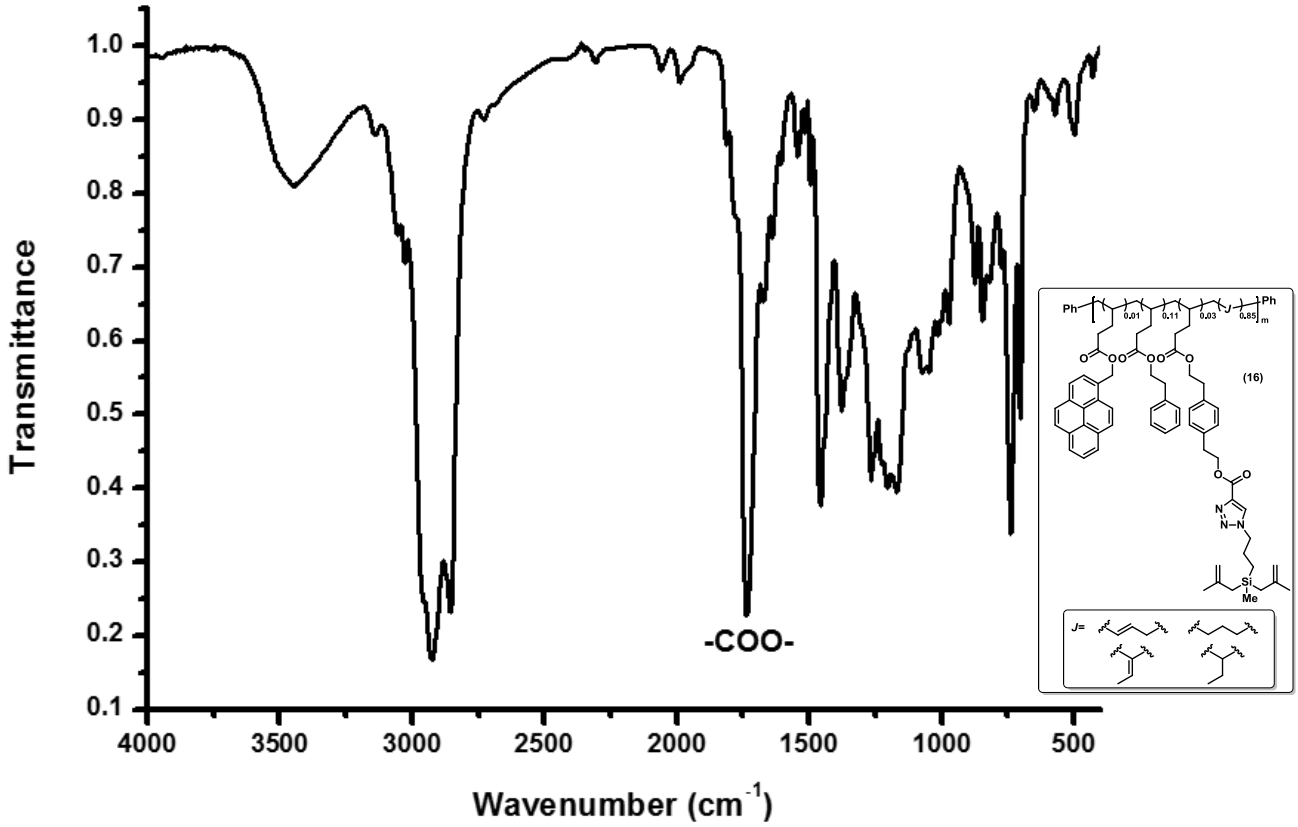

Transmittance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
-COO-
(7)


Transmittance
1.0
0.9
0.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
-COO-
(9)


Transmittance
1.0
0.9
0.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
-COO-
(12)


Transmittance
1.0
0.9
0.8
0.7
0.6
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
-COO-
(6b)


Transmittance
Wavenumber (cm-1)
-COO-
(6h)
OH
J=


Transmittance
Wavenumber (cm-1)
-COO-
(16)
J=