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Supporting Information

Precise Synthesis of Poly(macromonomer)s Containing Sugars by Repetitive ROMP and their Attachments to Poly(ethylene glycol): Synthesis, TEM Analysis and their Properties as Amphiphilic Block Fragments

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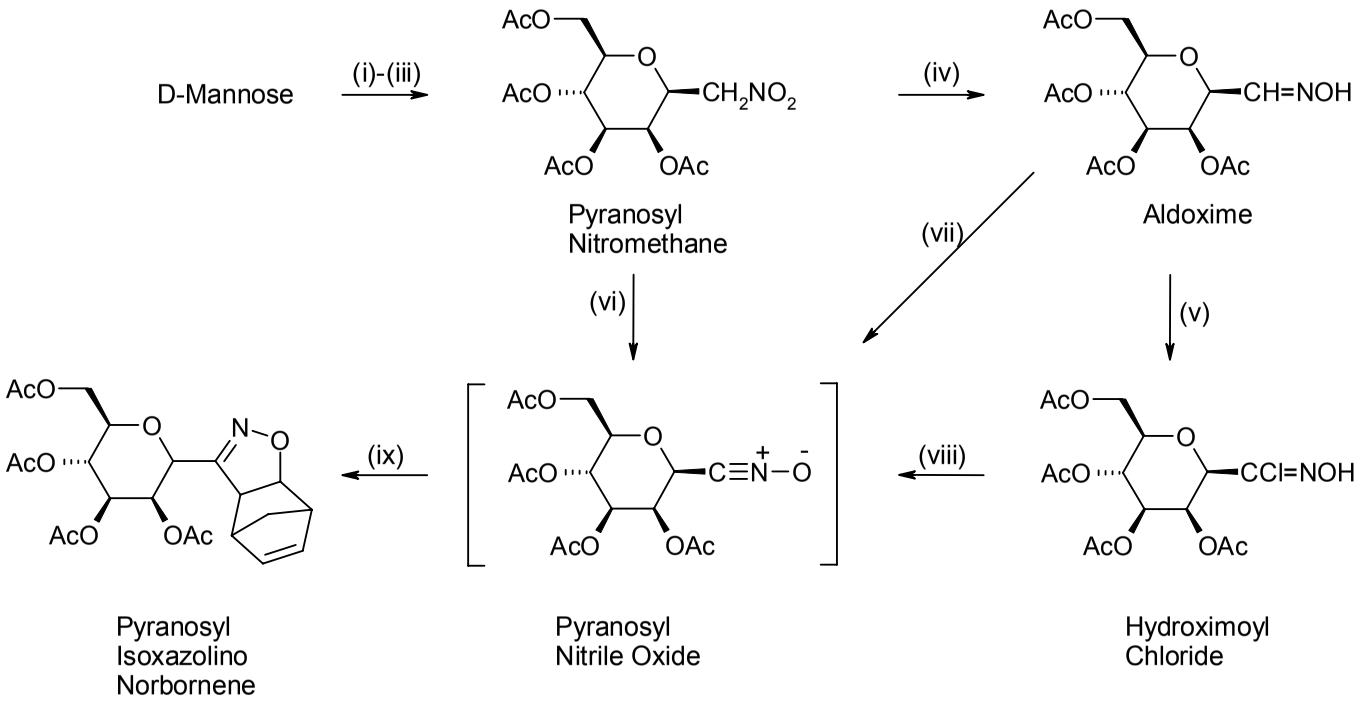
Contents

1. Generation and reaction of pyranosyl carbonitrile oxides.



Reagents: (i) $MeNO_2/NaOMe$; (ii) H_2O, reflux; (c) Ac_2O/CF_3SO_3H; (iv) $SnCl_2/PhSH/Et_3N$, THF; (v) Cl_2, CH_2Cl_2; (vi) TDI/Et_3N, PhMe, reflux, quench with $H_2NCH_2CH_2NH_2$; (vii) aq NaOCl, CH_2Cl_2; (viii) Et_3N, Et_2O; (ix) norbornadiene.

2. Synthetic procedures and identifications for macromonomer, poly(3a-d).

General. All chemicals used were of reagent grade and were purified by the standard purification procedures. Polymerization grade toluene was distilled from sodium and benzophenone, stored over sodium/potassium alloy in the drybox, and was then passed through an alumina short column prior to use. Anhydrous grade diethyl ether, dichloromethane, tetrahydrofuran (THF), and *n*-hexane (Kanto Kagaku Co. Ltd) were transferred into a bottle containing molecular sieves (mixture of 3A, 4A 1/16, and 13X), in the drybox. The molybdenum initiators of the type $(ArN)Mo(CHCMe_2Ph)(O^tBu)_2$ [Ar = 2,6-$^i Pr_2C_6H_3$ (**A1**)],[1] and 5-norbornene carboxylic acid chloride[2] were prepared according to the literature. The terminating agent 4-Me_3Si-C_6H_4CHO was prepared according to the previous report.[3]

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All ^1H- and ^{13}C-NMR spectra were recorded on a *JEOL* JNM-LA400 spectrometer (^1H, 399.65 MHz; ^{13}C, 100.40 MHz), and were obtained in the solvent indicated at 25 ºC, with all chemical shifts quoted in ppm and referenced to $SiMe_4$. HPLC grade THF (Wako Pure Chemical Industries, Inc.) was used for GPC and was degassed prior to use. GPC were performed at 40 ºC on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mmϕ) were calibrated versus polystyrene standard samples.

Syntheses of monomers. Polymerization grade of 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranos-6-*O*-yl 5-norbornene carboxylate (**a**) and 3,4-*O*-isopropylidene-α-D-ribonic-γ-lactone 5-norbornene carboxylate (**b**) were prepared from 2-norbornene-5-carboxylic acid chloride (mixture of *endo*/*exo* = 87/13) and the corresponding

commercially available acetal-protected sugars in the presence of triethylamine according to the previous report.[4] Syntheses of *exo*-3-(2',3',4')-tri-*O*-acetyl-β-D-xylopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole (**c**), *exo*-3-(2',3',4',5')-tetra-*O*-acetyl-β-D-mannopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole (**d**) were also according to the previous report.[5]

Poly(1a): Synthesis of block copolymers of norbornene (NBE) and 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranos-6-*O*-yl 5-norbornene-2-carboxylate.[4,6] The synthetic procedure for poly(**1a**) was according to our previous report.[6] A toluene solution of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)(O^{t}Bu)_2$ (**A1**, 2-7 mg/0.3-1.0 mL of toluene) was added in one portion to a rapidly stirred toluene solution (2-5 mL) containing the norbornene derivative (**a**) in toluene at room temperature, and the solution was stirred for the prescribed time. The second monomer (norbornene) in toluene (1.5 mL) was then added in one portion and the reaction mixture was further stirred for the additional required time. The polymerization was quenched by adding 4-trimethylsiloxybenzaldehyde (~10 mg). The solvents were removed *in vacuo* after 1 hour, and the resultant solid was dissolved in the minimum amount of THF. The solution was poured dropwise into methanol to afford pale white precipitates, and the copolymer, poly(**1a**) was collected by filtration and dried *in vacuo*. Yield > 95%. ^{1}H NMR ($CDCl_3$): δ 5.37-5.18 (br, olefinic H, 4H), 5.49 (br s), 4.58 (br s), 4.29-4.21 (br d), 3.97 (br s) (sugar group protons, 7 H), 2.93 (br), 2.75 (br), 2.40 (br), 1.95-1.74 (br) (protons of five-membered ring, 15 H), 1.54, 1.46, 1.41, 1.34, 1.31 (5xbs, 4xCH_3, 12 H), 0.24 (s, $Si(CH_3)_3$, 9 H). In addition to the above resonances, peaks at δ 7.51 (br s), 7.32-7.16, 6.75 (br), 6.26 (m), 6.04 (m), 5.58 (m) ppm were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 174.4 (C=O), 133.8-132.8 (C=C), 109.5, 108.7 (2×CMe_2),

96.2, 71.0-70.4, 65.9, 63.2-62.9 (sugar group), 48.4, 45.7, 43.4-42.1, 38.5, 33.1-32.1 (five-membered ring), 26.0, 24.9, 24.5 (4×CH_3).

Poly(1b): Synthesis of block copolymers of norbornene (NBE) and 3,4-*O*-isopropylidene-α-D-ribonic-γ-lactone 5-norbornene-2-carboxylate. Preparation analogous to that described above afforded poly(**1b**) as white precipitates. Yield 96-98 %. ^{1}H NMR ($CDCl_3$): δ 5.39-5.16 (br, olefinic H, 4 H), 5.49 (br m), 4.74-4.67 (br m), 4.29-4.10 (br m) (sugar group protons, 5 H), 2.86-2.76 (br d), 2.41 (br s), 1.94-1.67 (br m) (protons of five-membered rings, 15 H), 1.45, 1.36, 1.35, 1.34 (4×bs, 2×CH_3, 6 H), 0.22 (s, $Si(CH_3)_3$, 9 H). In addition to the above resonances, peaks at δ 7.51 (br s), 7.32-7.10 (m), 6.97 (m), 6.75 (m), 6.26 (m), 5.58 (br) ppm were also observed as tinay trace. ^{13}C NMR ($CDCl_3$): δ 175.4, 175.2 (C=O), 135.6, 134.9, 134.7 (C=C), 114.4 (CMe_2), 104.7, 80.1, 79.6, 77.7, 75.2, 65.2 (sugar group), 45.2, 44.8, 43.8, 43.1, 40.1, 34.6, 34.0, 33.9, 28.6, 28.6, 28.5 (five-membered rings), 27.4, 27.3 (2×CH_3), 1.9 ($Si(CH_3)_3$).

Poly(1a-b): Synthesis of triblock copolymers of nobornene (NBE), 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranos-6-*O*-yl 5-norbornene-2-carboxylate and 3,4-*O*-isopropylidene-α-D-ribonic-γ-lactone 5-norbornene-2-carboxylate. Preparation analogous to that described above afforded poly(**1a-b**) as white precipitates. Yield 98 %. ^{1}H NMR ($CDCl_3$): δ 5.41-5.20 (br, olefinic H, 4 H), 5.51 (br s), 4.86-4.69 (m), 4.59 (br s), 4.31-4.21 (br d), 4.08 (br), 3.99 (br s) (sugar group protons, 13 H), 2.93 (br), 2.79 (br), 2.43 (br), 1.97-1.70 (br), 1.05-0.97 (br) (protons of five-membered rings, 22 H), 1.53, 1.48, 1.44, 1.39, 1.37, 1.33 (6×bs, 6×CH_3, 18 H), 0.27 (s, $Si(CH_3)_3$, 9 H). In addition to the above resonances, peaks at δ 7.35-7.16 (m), 6.78 (m or d), 6.28 (m), 6.07 (m), 5.59 (m) were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 174.6, 174.5, 174.4 (C=O), 134.9-130.7 (C=C), 129.3, 128.0, 126.9 (end groups)

113.6, 109.5, 108.7 (3×CMe_2), 96.3, 79.7, 76.7, 75.3, 71.0, 70.7, 70.4, 65.9, 63.4-62.9, (sugar group), 48.4, 47.7, 45.7, 45.4, 43.4-42.1, 39.6, 38.6, 38.4, 35.8, 35.5, 33.1-32.2 (five-membered ring), 26.8, 26.1, 26.0, 25.8, 25.0, 24.5 (6×CH_3).

Poly(1c): Synthesis of block copolymers of norbornene (NBE) and *exo*-3-(2',3',4')-tri-*O*-acetyl-β-D-xylopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole. Procedure analogous to that described above afforded poly(**1c**). Yield 99 %. ^{1}H NMR ($CDCl_3$): δ 5.57-5.18 (br, olefinic H, 4H) 4.89 (br) (sugar group proton, 1 H), 4.75 (m, H-7a, 1 H), 4.29 (br), 4.20 (br), 4.13 (br), 3.85 (br), 3.30 (br) (sugar group protons, 5 H), 3.58 (br, H-3a, 1 H), 2.95 (br), 2.75 (br), 2.54 (br), 2.39 (br), 1.84-1.68 (br m), 1.40 (bs), 1.16-0.97 (br) (protons of five membered rings, 14 H), 2.06-1.96 (3×bs, 3×$COCH_3$, 9 H), 0.23 (s, $Si(CH_3)_3$, 9 H). In addition to the above resonances, peaks at 7.39-7.09 (m), 6.74 (br d or m), 6.25 (m), 6.00 (m) were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 170.0, 169.5 (3×$\underline{C}OCH_3$), 155.8 (C=N), 133.7-125.9 (olefinic carbons), 91.1 (C-7a), 74.4, 73.1, 69.8, 66.5 (sugar group carbons), 58.3 (C-3a), 50.5, 46.2, 43.2, 42.9, 42.6, 41.9, 41.2, 40.1, 38.4, 38.2, 32.9, 32.7, 32.0 (five membered rings), 20.5 (3×CO$\underline{C}H_3$).

Poly(1d): Synthesis of block copolymers of norbornene (NBE) and *exo*-3-(2',3',4',5')-tetra-*O*-acetyl-β-D-mannopyranosyl-3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole. Procedure analogous to that described above afforded poly(**1d**). Yield 99 %. ^{1}H NMR ($CDCl_3$): δ 5.72-5.20 (br, olefinic H, 4 H), 5.09 (br, sugar group proton, 1 H), 4.72 (m, H-7a, 1 H), 4.47 (br), 4.31 (br), 4.20 (br), 4.11 (br), 3.73 (br) (sugar group protons, 5 H), 3.47 (br) (H-3a), 2.79 (br), 2.58 (br), 2.43 (br), 12 H), 1.89-1.76 (br m), 1.35 (bs), 1.10-1.01 (br) (protons of five membered rings, 14 H), 2.08-1.97 (4xbs, 4×$COCH_3$, 12H), 0.26 (s, $Si(CH_3)_3$, 9 H). In addition to the above resonances, peakes at δ 7.34-7.12 (m), 6.78 (m), 6.40 (m), 6.24 (m), 6.00 (m)

were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 170.6, 170.1, 169.6 (4×$\underline{C}OCH_3$), 155.5 (C=N), 133.8-130.26 (olefinic carbons), 90.8 (C-7a), 73.8, 72.1, 71.8, 68.0, 65.9, 62.7 (sugar group carbons), 58.6 (C-3a), 50.5, 46.9, 43.4, 43.0, 42.7, 42.0, 41.3, 38.6, 38.4, 33.1, 32.9, 32.2 (five membered rings), 20.7 (4×CO$\underline{C}H_3$).

As reported previously,[4-7] the resultant ring-opened polymers, poly(**1a-d**), possessed a mixture of *cis* and *trans* olefinic double bonds and probably possessed a mixture of head-to-head, head-to-tail and tail-to-tail arrangement of the repeat unit.

Poly(2a): Removal of TMS protection from copolymer terminus.[6] The synthetic procedure for poly(**2a**) by hydrolysis of TMS group was according to the previous report.[3a] Into a rapidly stirred THF solution (5-10 mL) containing the copolymer was added 0.5M HCl, one drop/10 mgs poly(**2a**), and the mixture stirred for 1 hour at room temperature. The reaction solution was then added dropwise into methanol to isolate the end group deprotected copolymer, poly(**2a**) which was collected by filtration and dried *in vacuo*. Yield >99 %. ^1H NMR ($CDCl_3$): δ 5.37-5.17 (br, olefinic H, 4 H), 5.49 (br s), 4.58 (br s), 4.28-4.20 (br d), 3.97 (br) (sugar group protons, 7 H), 2.93-2.76 (br d), 2.40 (br s), 1.86-1.74 (br) (protons of five-membered rings, 15 H), 1.47, 1.41, 1.34, 1.30 (4×bs, 4×CH_3, 12 H). ^{13}C NMR ($CDCl_3$): δ 174.6 (C=O), 134.6-129.3 (C=C), 109.5, 108.7 (2×CMe_2), 96.2, 70.9-70.6, 67.9, 65.8, 62.8 (sugar group), 48.3, 45.8, 43.4-42.1, 38.4, 36.0, 32.9-32.2 (five-membered rings), 26.0, 25.6, 25.0, 24.5 (4×CH_3).

Poly(2b): Removal of TMS protection from copolymer terminus. Procedure analogous to that described above afforded poly(**2b**). Yield 98-99 %. ^1H NMR ($CDCl_3$): δ 5.32-5.17 (br, olefinic H, 4H), 5.39 (br m), 4.82-4.67 (br m), 4.29-4.16 (br m) (sugar group protons, 5 H), 2.79-2.76 (br d), 2.39 (br s), 1.94-1.70 (br m) (protons of five-membered rings, 15 H), 1.46, 1.37, 1.35, 1.34 (4×bs, 2×CH_3, 6 H). In addition

to the above resonances, peaks at δ 7.59 (br), 7.35-7.16 (m), 6.78 (m or d), 6.28 (m), 6.07 (m), 5.59 (m) were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 174.1, 173.6, 173.4 (C=O), 149.9 (phenoxy), 133.9-133.7, 133.1-132.8, 130.7, 128.0, 127.1, 126.1 (C=C), 115.3, 113.6 (CMe_2), 101.2, 79.7, 79.5, 77.8, 75.2, 63.4 (sugar group), 48.3, 47.7, 45.3, 43.6-42.7, 42.0, 41.3, 38.9, 38.6, 38.4, 35.3, 33.0-32.2 (five-membered rings), 26.7, 25.8, 25.6 (2×CH_3).

Poly(2a-b): Removal of TMS protection from copolymer terminus. Procedure analogous to that described above afforded poly(**2a-b**). Yield 99 %. ^{1}H NMR ($CDCl_3$): δ 5.38-5.17 (br, olefinic H, 4 H), 5.47 (br s), 4.82-4.66 (m), 4.56 (br s), 4.27-4.19 (br d), 4.08 (br), 3.96 (br s) (sugar group protons, 12 H), 2.89 (br), 2.75 (br), 2.39 (br), 1.93-1.69 (br), 1.05-0.97 (br) (protons of five-membered rings, 22 H) 1.49, 1.44, 1.39, 1.35, 1.33, 1.29 (6×bs, 6×CH_3, 18 H). In addition to the above resonances, peaks at δ 7.36-7.10 (m), 6.77 (m), 6.25 (m), 6.05 (m), 5.57 (m) were also observed as tiny trace. ^{13}C NMR ($CDCl_3$): δ 174.6, 174.5, 174.4 173.6 (C=O), 134.8-130.7 129.4, 128.0, 126.9 (aromatic and olefinic end groups) 113.6, 109.5, 108.7 (3×CMe_2), 96.2, 79.7, 76.7, 75.2, 71.0, 70.6, 70.4, 65.8, 63.4-62.9, (sugar group), 48.1, 47.7, 45.7, 45.4, 43.4-42.0, 39.6, 39.0, 38.6, 38.4, 35.8, 35.5, 33.0-32.1 (five-membered rings), 26.7, 25.9, 25.7, 25.6, 25.0, 24.5 (6×CH_3).

Poly(2c): Removal of TMS protection from copolymer terminus. Procedure analogous to that described above afforded poly(**2c**). Yield 98 %. ^{1}H NMR ($CDCl_3$): δ 5.57-5.18 (br, olefinic H, 6 H) 4.91 (br) (sugar group proton, 1 H), 4.75 (m, H-7a, 1-H), 4.29 (br), 4.20 (br), 4.13 (br), 3.85 (br), 3.32 (br) (sugar group protons, 5 H), 3.58 (br) (H-3a), 2.99 (br), 2.75 (br), 2.56 (br), 2.39 (br), 1.84-1.68 (br m), 1.40 (bs), 1.16-0.97 (br) (protons of five membered rings, 15 H), 2.06-1.96 (3×bs, 3×$COCH_3$). ^{13}C NMR ($CDCl_3$): δ 170.1, 169.5 (3×$\underline{C}OCH_3$), 155.6 (C=N), 133.6-125.9 (olefinic

carbons), 91.2 (C-7a), 74.4, 73.1, 69.8, 66.5 (sugar group carbons), 58.3 (C-3a), 50.5, 46.2, 43.4, 42.9, 42.6, 42.0, 41.2, 40.1, 38.4, 38.2, 32.9, 32.9, 32.0 (five membered rings), 20.4 (3×CO<u>C</u>H_3).

Poly(2d): Removal of TMS protection from copolymer terminus. Procedure analogous to that described above afforded poly(**2d**). Yield 98 %. ^{1}H NMR ($CDCl_3$): δ 5.72-5.21 (br, olefinic H, 4 H), 5.08 (br, sugar group proton, 1 H), 4.72 (m) (H-7a), 4.48 (br), 4.30 (br), 4.20 (br), 4.10 (br), 3.74 (br) (sugar group protons, 7 H), 3.48 (br, H-3a, 1 H), 2.79 (br), 2.58 (br), 2.43 (br), 1.89-1.73 (br m), 1.35 (bs), 1.09-0.93 (br) (protons of five membered rings, 14 H), 2.08-1.97 (4×bs, 4×$COCH_3$, 12 H). ^{13}C NMR ($CDCl_3$): δ 170.6, 170.1, 169.5 (4x<u>C</u>OCH_3), 155.5 (C=N), 133.8-128.2 (olefinic carbons), 125.4, 115.9 (end group carbons), 91.0 (C-7a), 73.7, 71.8, 68.0, 65.9, 62.7 (sugar group carbons), 58.7 (C-3a), 50.5, 46.9, 43.3, 43.0, 42.0, 41.3, 38.5, 38.3, 34.2, 32.9, 32.1, 30.3, 28.8 (five membered rings), 20.7 (4×CO<u>C</u>H_3).

Poly(3a): Preparation of macromonomer. The basic synthetic procedure for synthesis for poly(**3a**) was analogous to that for norbornene containing ring-opened poly(norbornene) in the previous report.[3,7] The deprotected polymer, poly(**2a**), and Et_3N (ca. 1.1 equivs. to the polymer based on the M_n value calculated by the initial monomer/initiator molar ratio) were dissolved in THF, and norbornene carboxylic acid chloride (1.5 equivs.) was then added dropwise. The reaction mixture was stirred for 2 hours at room temperature and was then refluxed for 5 hours. The mixture was then added dropwise into a cold methanol solution. The resultant precipitate was collected by filtration and dried *in vacuo*. The prepared macromonomer was further purified by passing through a column of alumina (as the toluene solution), in the drybox. Yield 98-99 %. ^{1}H NMR ($CDCl_3$): δ 7.29-7.19 (m), 6.87 (d, J = 8.4 Hz) 6.27 (d, J = 15.7 Hz), 6.04 (m, NBE olefinic protons), 5.37-5.17 (br, polymer olefinic

protons, 4 H), 5.49 (br s), 4.58 (br s), 4.28-4.02 (br d), 3.96 (br s) (sugar group protons, 7 H), 3.78 (br s), 3.51 (d, J = 8.4 Hz), 3.38 (m, NBE non-olefinic protons, H-7), 3.09 (br), 2.92 (br), 2.75 (br), 2.39 (br), 1.94-1.21 (m, protons of five membered ring, 15-H), 1.01, 0.99, 0.98, 0.96 (4×bs, 4×CH_3, 12 H). ^{13}C NMR ($CDCl_3$): δ 174.5 (C=O), 149.8 (phenoxy), 137.7, 135.4, 134.7 (norbornene olefinic), 133.9, 133.1-132.8, 130.7, 129.4, 127.9, 126.7, 126.0, 125.6, 121.4 (polymer olefinic), 109.5, 108.6 (2×CMe_2), 96.2, 70.9, 70.4, 65.8, 63.1, 62.8 (sugar group), 49.6, 48.2, 45.6, 43.4, 43.0, 42.7, 42.0, 41.3, 40.7, 40.1, 39.6, 38.6, 38.4, 37.7, 36.1, 33.1, 32.3, 32.1, 29.2 (non olefinic), 25.9, 24.9, 24.5 (4×CH_3).

Poly(3b): Preparation of macromonomer. Preparation analogous to that described above afforded the macromonomer, poly(**3b**), as white precipitates. Yield 98-99 %. ^{1}H NMR ($CDCl_3$): δ 7.29-7.19 (m), 6.59 (d, J = 1.7 Hz), 6.54 (td, J = 3.2, 1.2 Hz), 6.33-6.09 (m), 6.04 (m, NBE olefinic H, 2 H), 5.40 (br s), 5.35 (br s), 5.31-5.30 (br m), 5.18-5.16 (br d, polymer olefinic H, 4 H), 5.95-6.15 (br), 5.63 (br), 4.83 (br s), 4.74 (br s), 4.68-4.67 (br), 4.29-4.15 (br, sugar group protons, 5 H), 3.74-3.59 (m, NBE non olefinic protons, J = 8.4 Hz, 7 H), 3.18-2.76 (br m), 2.39 (br s), 1.94 (br), 1.86-1.69 (br m, protons of five membered rings, 15 H), 1.43, 1.35, 1.33, 1.32 (4xbs, 2×CH_3, 6 H). ^{13}C NMR ($CDCl_3$): δ 174.8, 174.1, 173.6 (C=O), 150.7 (phenoxy), 138.1, 136.6, 135.5, 134.7 (norbornene olefinic), 133.7, 136.6, 135.5, 134.7, 133.7-132.8, 130.6, 129.4, 128.0, 126.7, 126.0, 121.4 (polymer olefinic and aromatic), 113.6 (CMe_2), 101.5-100.4, 79.7, 77.7, 75.2, 63.4 (sugar group), 48.3, 47.7, 45.4, 43.4, 43.1, 42.7, 42.0, 41.3, 38.6, 38.3, 35.4, 33.0, 32.8, 32.3, 32.1, 28.8 (non olefinic), 26.7, 25.7, 25.6 (2×CH_3).

Poly(3a-b): Preparation of macromonomer. Preparation analogous to that described above afforded the macromonomer, poly(**3a-b**), as white precipitates. Yield

99 %. ^{1}H NMR ($CDCl_3$): δ 5.38-5.17 (br, polymer olefinic H, 4 H), 5.49 (br s), 4.83-4.67 (m), 4.58 (br s), 4.28-4.21 (br d), 4.08 (br), 3.97 (br s, sugar group protons, 5 H), 3.72-3.61 (m, NBE non olefinic protons, 7 H), 2.91 (br), 2.76 (br), 2.41 (br), 1.95-1.74 (br, protons of five-membered rings, 14 H), 1.50, 1.46, 1.41, 1.37, 1.34, 1.30 (6×bs, 6×CH_3, 18 H). ^{13}C NMR ($CDCl_3$): δ 174.6, 174.5, (C=O), 150.0 (phenoxy), 134.8, 134.3, 133.8 (NBE olefinic) 133.0-129.4 (polymer olefinic carbons), 128.0, 126.9 (end groups) 113.6, 109.5, 108.7 (3×CMe_2), 96.3, 79.6, 76.7, 75.2, 71.0, 70.7, 70.4, 65.9, 63.4-62.9, 60.6 (sugar group), 49.9, 48.0, 45.7, 43.4, 42.1, 41.3, 39.1-37.7, 36.0, 33.0-32.2 (non olefinic), 26.8, 26.0, 25.8, 25.0, 24.9, 24.5 (6×CH_3).

Poly(3c): Preparation of macromonomer. Preparation analogous to that described above afforded the macromonomer, poly(**3c**), as white precipitates. Yield 98 %. ^{1}H NMR ($CDCl_3$): δ 6.95 (br), 6.25 (br), 6.00 (m), 6.46 (bd), 6.41 (bd), 5.91 (m), 5.77 (m, NBE olefinic H, 2 H), 5.41-5.19 (br, polymer olefinic H, 4 H) 4.92 (br, sugar group proton, 1-H), 4.72 (m, H-7a, 1 H), 4.29 (br), 4.12 (br), 3.81 (br), 3.67-3.60 (br) (sugar group protons, 5 H), 3.46 (br, H-3a, 1 H), 3.01 (br), 2.77 (br), 2.41 (br), 2.24 (br), 1.77 (br m), 1.41-1.33 (bs), 1.00 (br, non olefinic protons, 21 H), 2.07-2.00 (3×bs, 3×$COCH_3$, 9 H). ^{13}C NMR ($CDCl_3$): δ 170.0, 169.5 (3×$\underline{C}OCH_3$), 155.8 (C=N), 152.9 (phenoxy), 135.8, 135.6, 134.9 (NBE olefinic), 133.8-130.26, 129.7, 128.9, 128.1 (olefinic and aromatic carbons), 133.7-125.9 (olefinic carbons), 91.1 (C-7a), 74.4, 73.1, 69.8, 66.5 (sugar group carbons), 58.3 (C-3a), 50.5, 46.2, 43.2, 42.9, 42.6, 41.9, 41.2, 40.1, 38.4, 38.2, 32.9, 32.7, 32.0 (five membered rings), 20.5 (3×CO$\underline{C}H_3$).

Poly(3d): Preparation of macromonomer. Preparation analogous to that described above afforded the macromonomer, poly(**3d**), as white precipitates. Yield 97-98 %. ^{1}H NMR ($CDCl_3$): δ 7.34-7.10 (m), 6.95 (m), 6.43 (bd), 6.00 (m), 6.26 (t, J = 3.1), 6.19 (q, J = 2.9), 6.08 (d, J = 3.3, NBE olefinic H, 2 H), 5.72-5.20 (br, polymer

olefinic H, 4 H) 5.08 (br, sugar group proton, 1 H), 4.72 (m, H-7a, 1 H), 4.31 (br), 4.20-4.10 (br), 4.17 (br), 3.73 (br), 3.30 (br, sugar group protons, 6 H), 3.63 (br, H-3a, 1 H), 2.98 (br), 2.79 (br), 2.58 (br), 2.33 (br), 1.89-1.69 (br m), 1.36 (bs), 1.09-0.99 (br, non olefinic protons, 21 H), 2.08-1.97 (4×bs, 4×$COCH_3$, 12 H). ^{13}C NMR ($CDCl_3$): δ 170.7, 170.2, 169.5 (4×$\underline{C}OCH_3$), 155.5 (C=N), 151.8 (phenoxy), 138.5, 138.1, 135.7, 135.6 (NBE olefinic), 133.8-130.3, 129.7, 128.9, 128.1 (olefinic and aromatic carbons), 91.0 (C-7a), 73.8, 72.5, 71.8, 68.0, 65.7, 62.7 (sugar group carbons), 58.6 (C-3a), 50.5, 46.8, 43.3, 43.1, 42.7, 42.0, 41.3, 38.6, 38.3, 33.0, 32.8, 32.1. 30.1 (five membered rings), 20.8, 20.7 (4×CO$\underline{C}H_3$).

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Table 2-1. Preparation of macromonomer, poly(**3a-b**).

run	monomer	poly(**1a-b**)				poly(**2a-b**)			poly(**3a-b**)				
	NBE/**a** or **b** (m/n)[a]	$M_{n(GPC)}$[b] $\times 10^{-4}$	$M_{n(calc)}$[c] $\times 10^{-4}$	$M_{n(NMR)}$[d] $\times 10^{-4}$	M_w/M_n[b]	$M_{n(GPC)}$[b] $\times 10^{-4}$	M_w/M_n[b]	yield[e] / %	$M_{n(GPC)}$[b] $\times 10^{-4}$	$M_{n(calc)}$[c] $\times 10^{-4}$	$M_{n(NMR)}$[d] $\times 10^{-4}$	M_w/M_n[b]	yield[e] / %
1	NBE/**a** (10/20)	1.17	0.85	0.93	1.10	1.15	1.11	99	1.18	0.85	0.94	1.12	97
2	NBE/**a** (20/20)	1.33	0.95	0.98	1.14	1.31	1.09	99	1.28	0.95	1.02	1.11	99
3	NBE/**a** (20/20)	1.25	0.95	0.96	1.11	1.29	1.10	98	1.33	0.95	1.03	1.13	98
4	NBE/**a** (25/25)	1.53	1.18	1.22	1.20	1.60	1.12	95	1.58	1.18	1.24	1.10	99
5	NBE/**a** (25/25)	1.57	1.18	1.25	1.12	1.54	1.09	99	1.58	1.18	1.24	1.10	99
6	NBE/**b** (20/20)	1.04	0.83	0.85	1.18	1.01	1.16	99	1.02	0.84	0.92	1.18	99
7	NBE/**b** (20/30)	1.43	1.14	1.18	1.16	1.41	1.16	99	1.40	1.15	1.24	1.16	98
8	NBE/**b**/**a** (20/20/20)	1.77	1.56	1.58	1.08	1.73	1.08	99	1.82	1.56	1.59	1.08	99

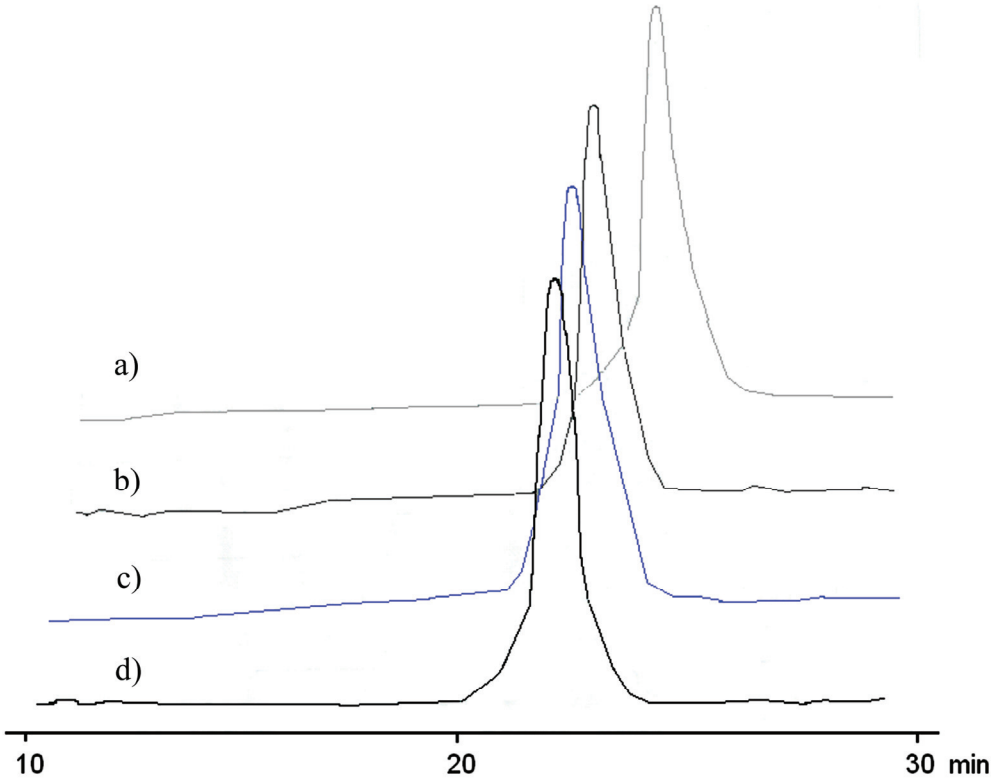
[a]Conditions: toluene (3.5 g) at 25 °C. [b]GPC data in THF vs polystyrene standards. [c]Calculated from initial feedstock ratios. [d]Estimated from ^{1}H NMR spectra. [e]Isolated yield.

Table 2-2. Preparation of isoxazoline functionalized macromonomer, poly(**3**).

run	monomer	poly(**1c-d**)				poly(**2c-d**)			poly(**3c-d**)				
	NBE/**c** or **d** (m/n)[a]	$M_{n(GPC)}$[b] $\times 10^{-4}$	$M_{n(calc)}$[c] $\times 10^{-4}$	$M_{n(NMR)}$[d] $\times 10^{-4}$	M_w/M_n[b]	$M_{n(GPC)}$[b] $\times 10^{-4}$	M_w/M_n[b]	yield[e] / %	$M_{n(GPC)}$[b] $\times 10^{-4}$	$M_{n(calc)}$[c] $\times 10^{-4}$	$M_{n(NMR)}$[d] $\times 10^{-4}$	M_w/M_n[b]	yield[e] / %
9	NBE/**c** (20/20)	1.06	1.00	1.01	1.18	0.94	1.17	98	1.08	1.00	1.02	1.15	98
10	NBE/**c** (25/25)	1.56	1.25	1.29	1.08	1.54	1.07	99	1.56	1.25	1.27	1.09	98
11	NBE/**d** (20/20)	1.26	1.15	1.16	1.10	1.24	1.08	99	1.27	1.15	1.18	1.09	98
12	NBE/**d** (30/30)	1.92	1.71	1.74	1.18	1.91	1.10	99	1.94	1.71	1.75	1.14	97

[a]Conditions: toluene (3.5 g) at 25 °C. [b]GPC data in THF vs polystyrene standards. [c]Calculated from initial feedstock ratios. [d]Estimated from ^{1}H NMR spectra. [e]Isolated yield.

3. GPC traces for selected macromonomer and poly(macromonomer)s



a) Macromonomer, poly(**3a**) [repeating unit: NBE_{20}-*b*-$\mathbf{a}_{20}$]; M_n = 1.28 x10^4; M_w/M_n = 1.11.

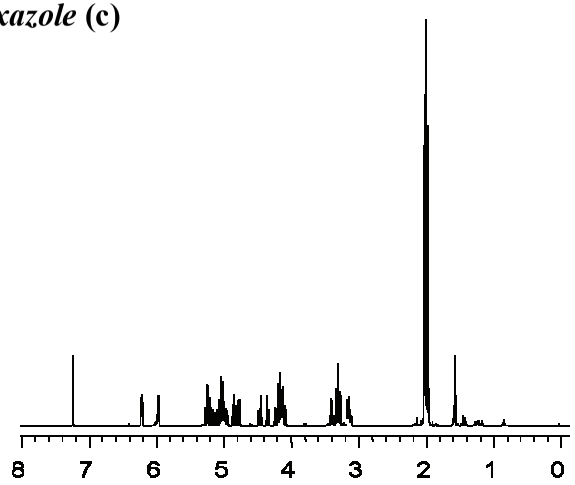
b) Poly(macromonomer), poly(**4a**); M_n = 3.99 x10^4; M_w/M_n = 1.19; DP_n = 3.1; run 7.

c) Poly(macromonomer) , poly(**4a**); M_n = 5.87 x10^4; M_w/M_n = 1.09; DP_n = 4.6; run 6.

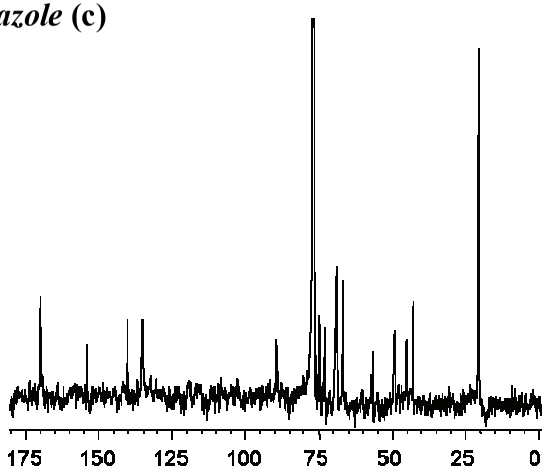
d) Poly(macromonomer); M_n = 11.76 x10^4; M_w/M_n = 1.07; DP_n = 9.2; run 5.

4. ^{1}H and ^{13}C NMR spectra for poly(1) - poly(8).

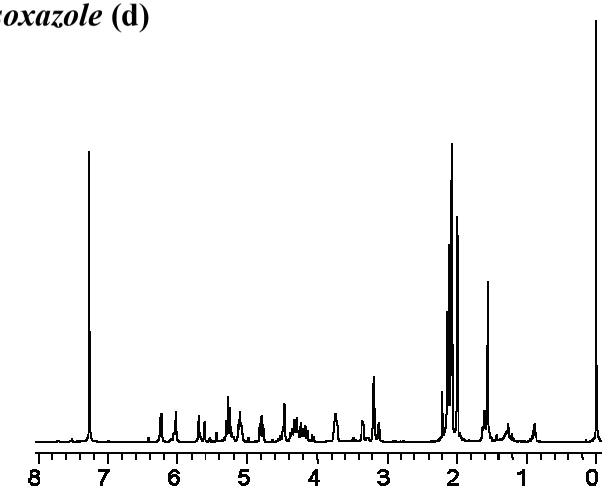
^{1}H NMR spectrum (in $CDCl_3$) for *exo-3-(2',3',4')-tri-O-acetyl-β-D-xylopyranosyl- 3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole* (c)



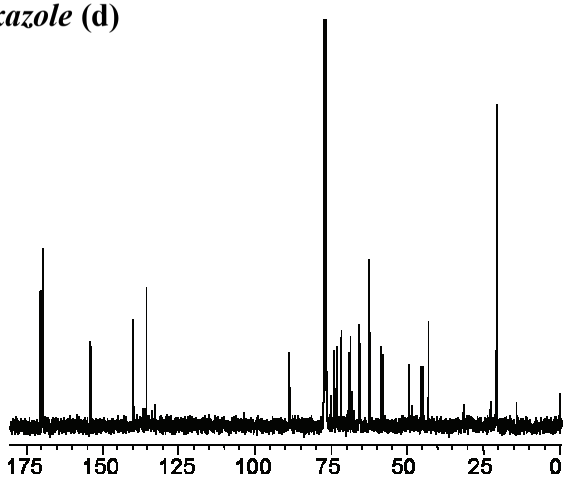
^{13}C NMR spectrum (in $CDCl_3$) for *exo-3-(2',3',4')-tri-O-acetyl-β-D-xylopyranosyl- 3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole* (c)



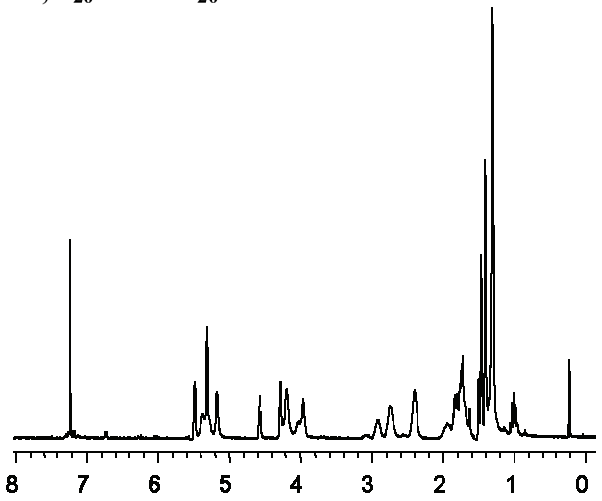
^{1}H NMR spectrum (in $CDCl_3$) for *exo*-3-(*2',3',4',5')-tetra-O-acetyl-β-D-mannopyranosyl- 3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole* (d)



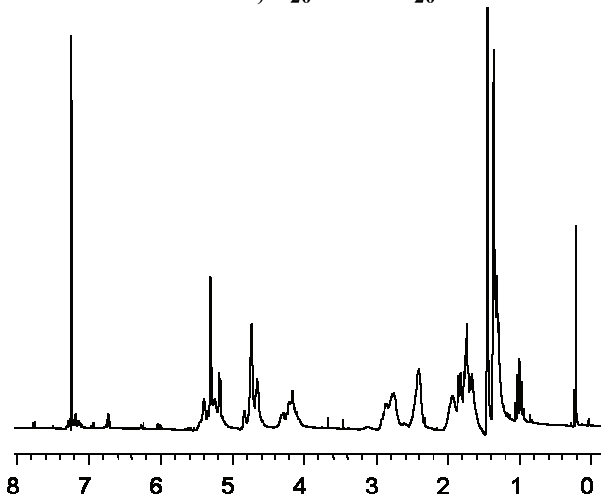
^{13}C NMR spectrum (in $CDCl_3$) for *exo*-3-(*2',3',4',5')-tetra-O-acetyl-β-D-mannopyranosyl- 3a,4,7,7a-tetrahydro-4,7-methano-benzo[d]isoxazole* (d)



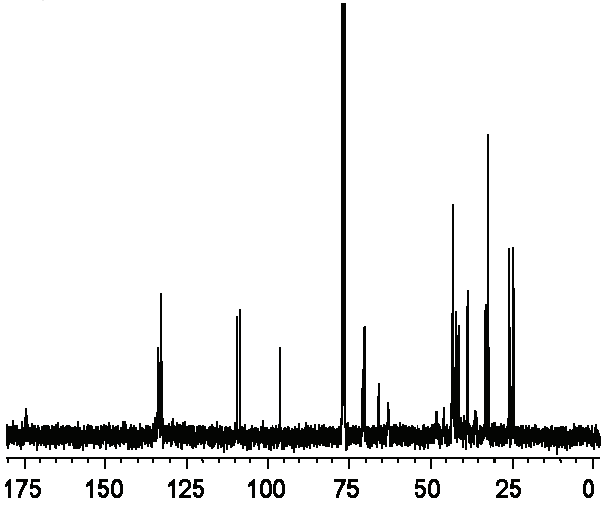
^{1}H NMR spectrum (in $CDCl_3$) for poly(1a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-OTMS



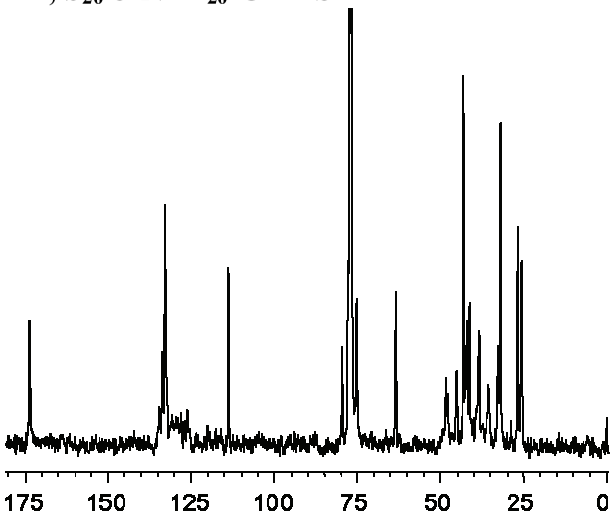
^{1}H NMR spectrum (in $CDCl_3$) for poly(1b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-OTMS



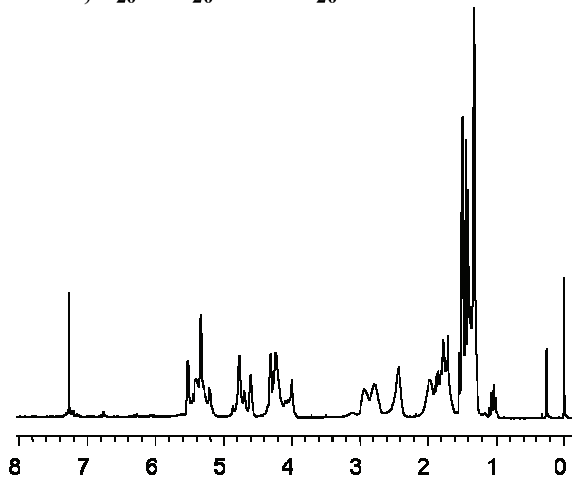
^{13}C NMR spectrum (in $CDCl_3$) for poly(1a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-OTMS



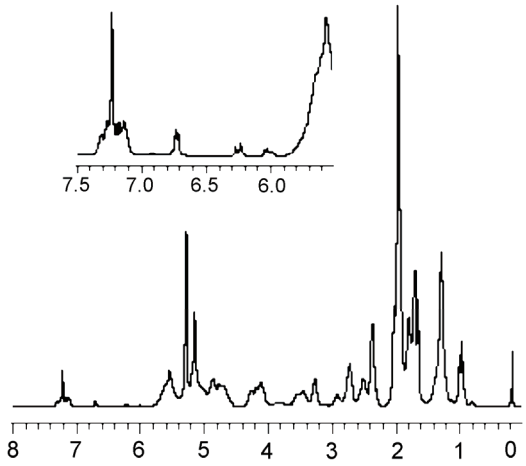
^{13}C NMR spectrum (in $CDCl_3$) for poly(1b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-OTMS



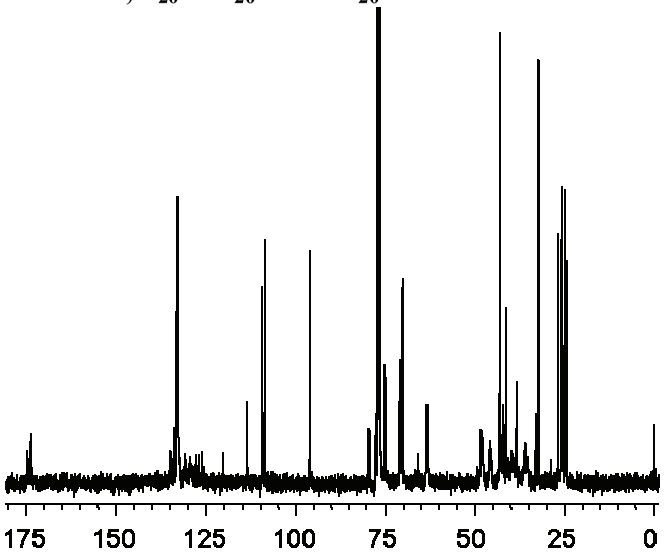
^{1}H NMR spectrum (in $CDCl_3$) for poly(1a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-OTMS



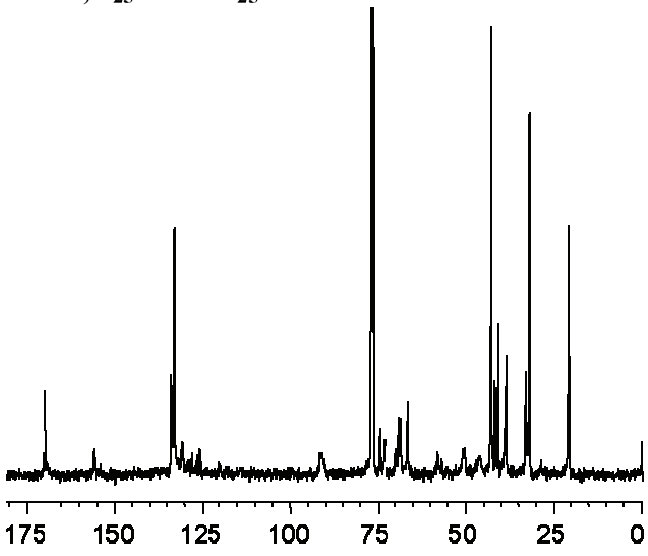
^{1}H NMR spectrum (in $CDCl_3$) for poly(1c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-OTMS



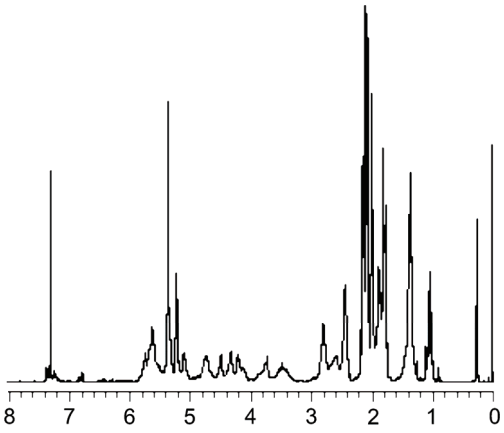
^{13}C NMR spectrum (in $CDCl_3$) for poly(1a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-OTMS



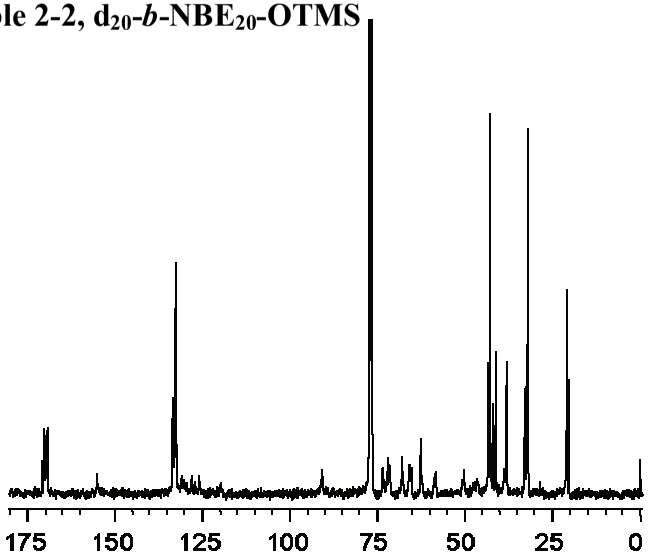
^{13}C NMR spectrum (in $CDCl_3$) for poly(1c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-OTMS



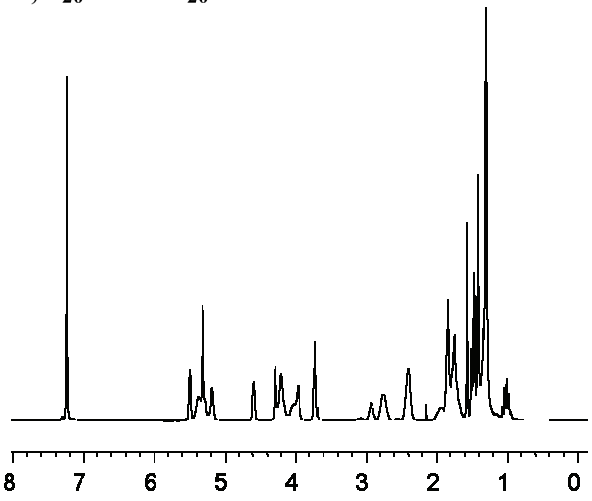
^{1}H NMR spectrum (in $CDCl_3$) for poly(1d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-OTMS



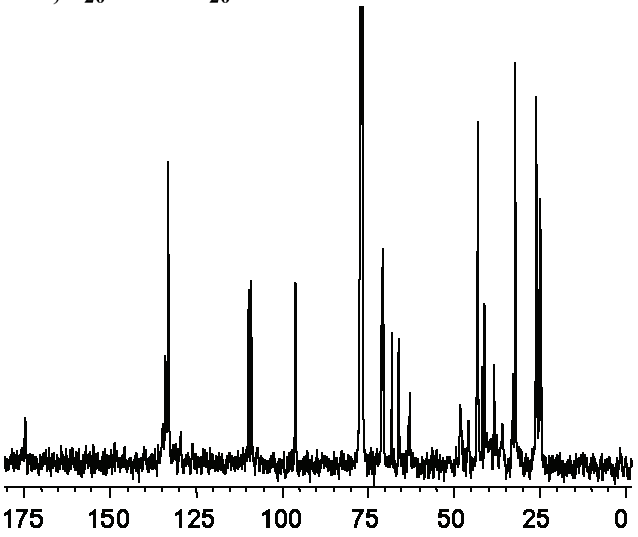
^{13}C NMR spectrum (in $CDCl_3$) for poly(1d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-OTMS



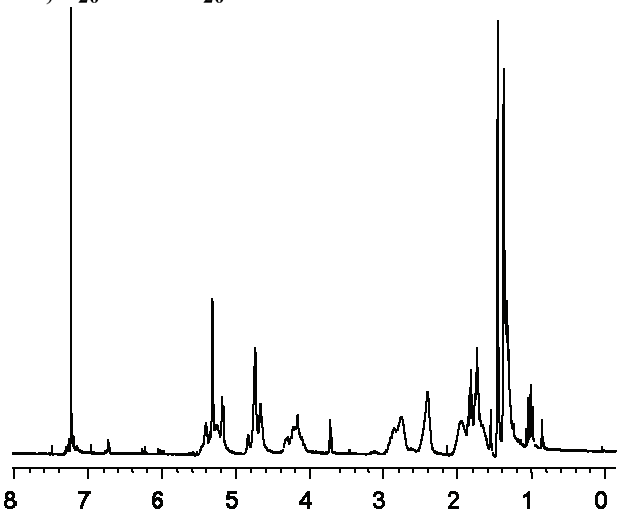
^{1}H NMR spectrum (in $CDCl_3$) for poly(2a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-OH



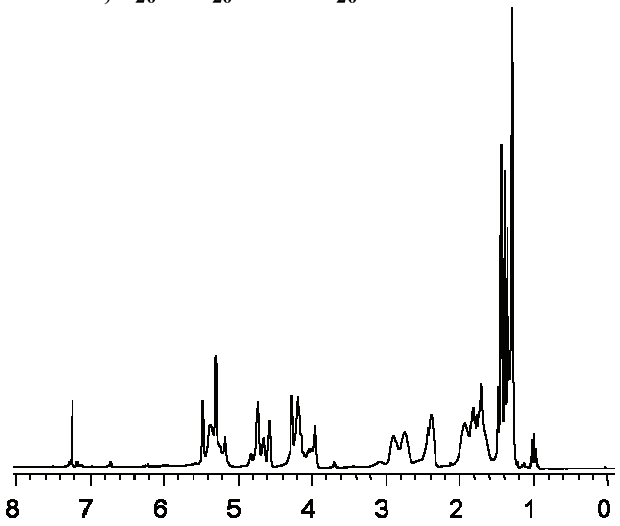
^{13}C NMR spectrum (in $CDCl_3$) for poly(2a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-OH



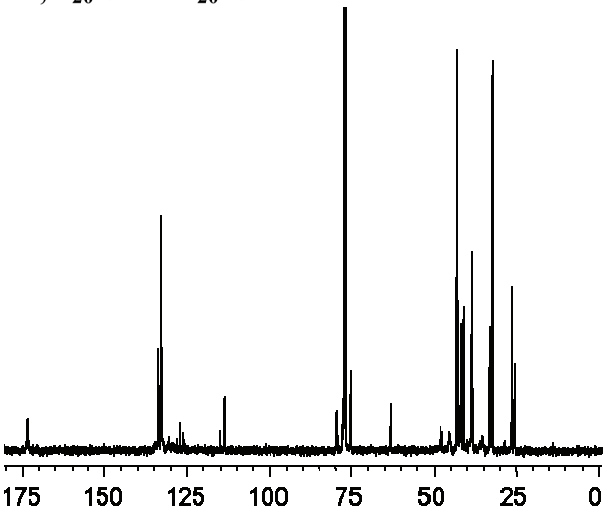
^{1}H NMR spectrum (in $CDCl_3$) for poly(2b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-OH



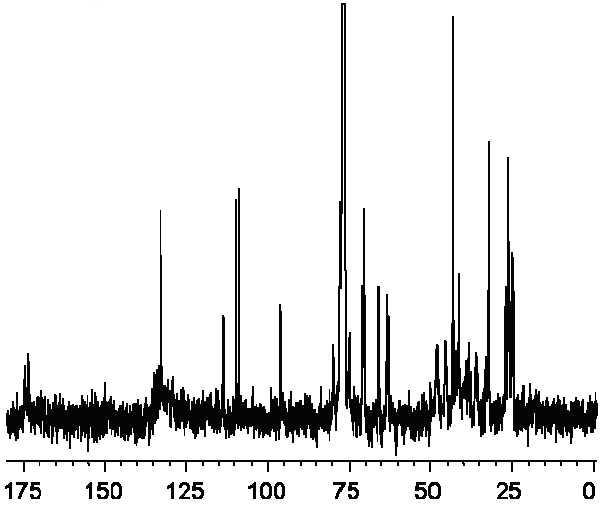
^{1}H NMR spectrum (in $CDCl_3$) for poly(2a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-OH



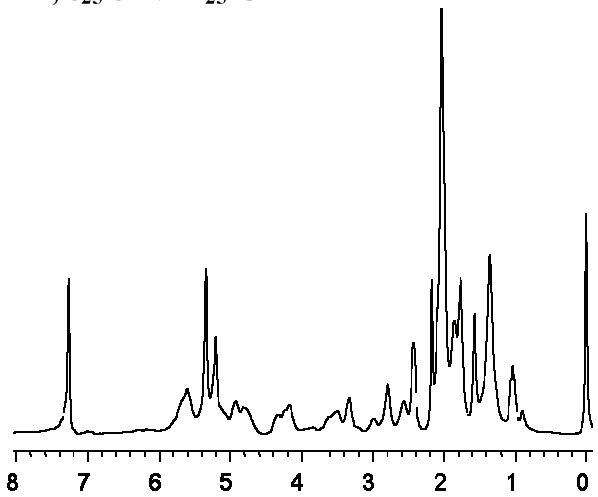
^{13}C NMR spectrum (in $CDCl_3$) for poly(2b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-OH



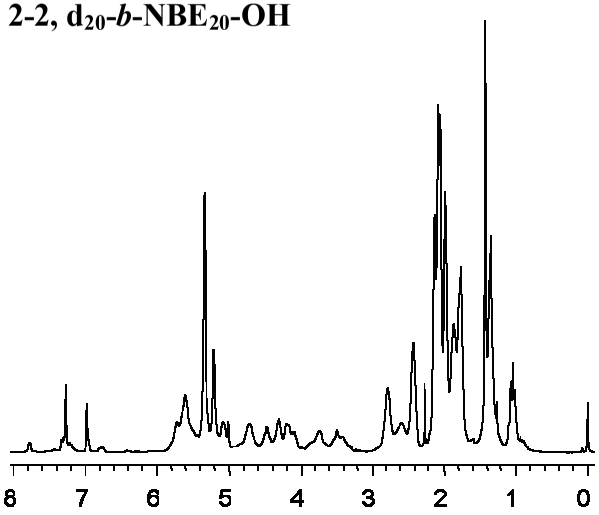
^{13}C NMR spectrum (in $CDCl_3$) for poly(2a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-OH



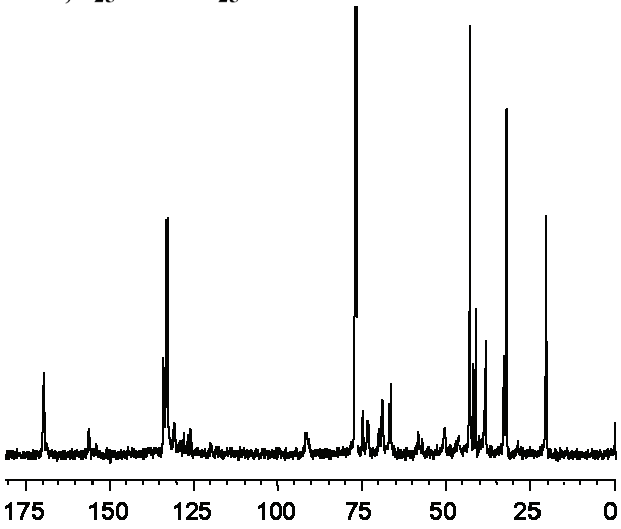
^{1}H NMR spectrum (in $CDCl_3$) for poly(2c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-OH



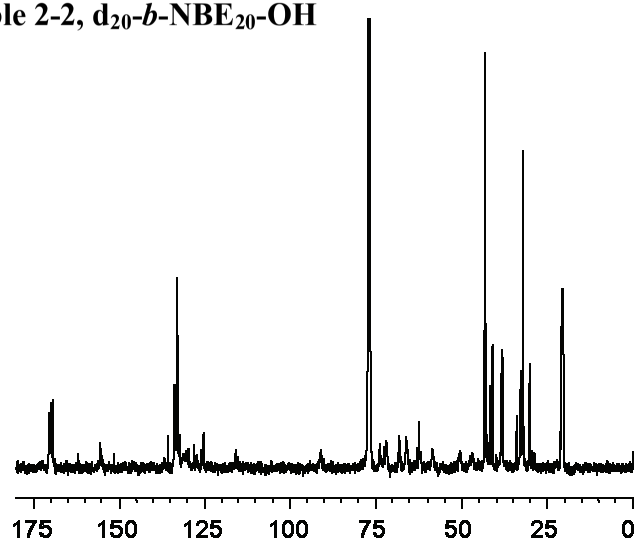
^{1}H NMR spectrum (in $CDCl_3$) for poly(2d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-OH



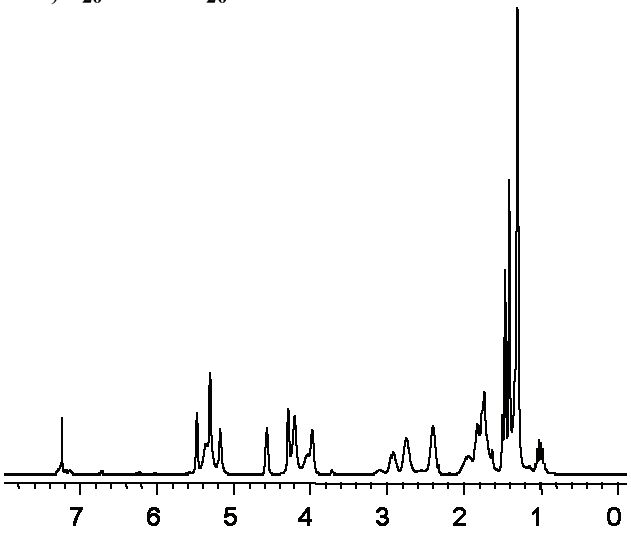
^{13}C NMR spectrum (in $CDCl_3$) for poly(2c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-OH



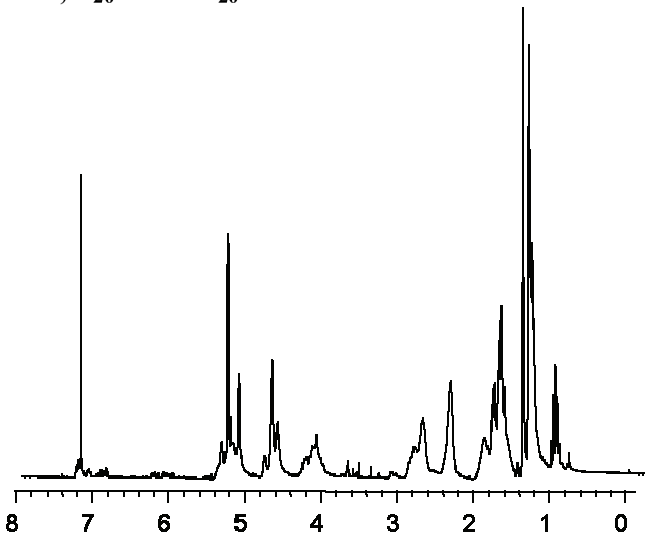
^{13}C NMR spectrum (in $CDCl_3$) for poly(2d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-OH



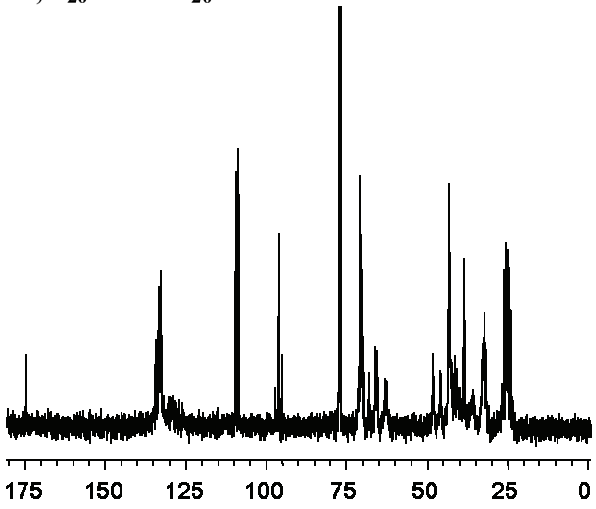
^{1}H NMR spectrum (in $CDCl_3$) for poly(3a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-ONBE



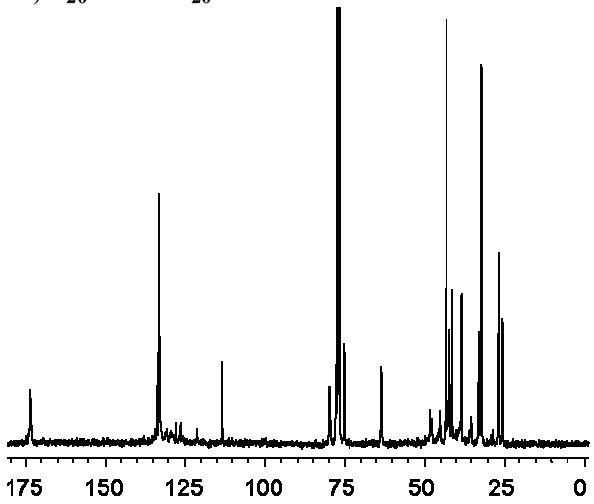
^{1}H NMR spectrum (in $CDCl_3$) for poly(3b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-ONBE



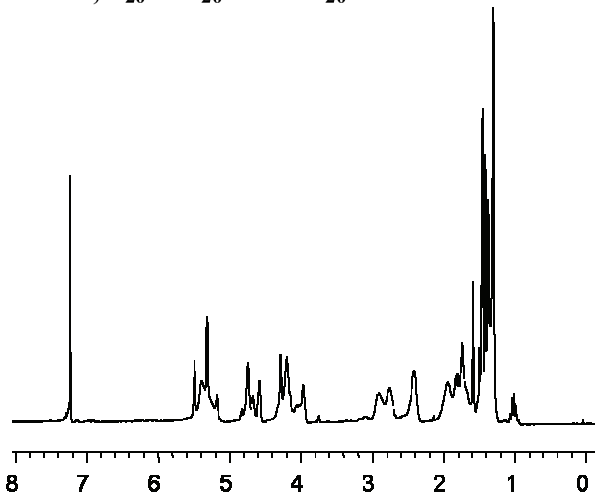
^{13}C NMR spectrum (in $CDCl_3$) for poly(3a), corresponding to run 2 in Table 2-1, a_{20}-*b*-NBE_{20}-ONBE



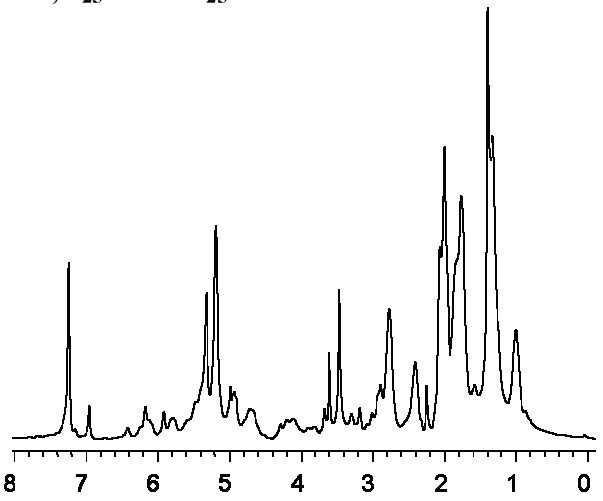
^{13}C NMR spectrum (in $CDCl_3$) for poly(3b), corresponding to run 6 in Table 2-1, b_{20}-*b*-NBE_{20}-ONBE



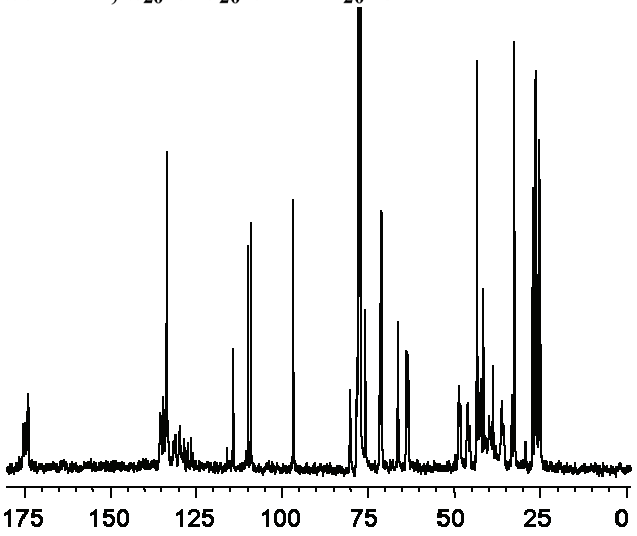
^{1}H NMR spectrum (in $CDCl_3$) for poly(3a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-ONBE



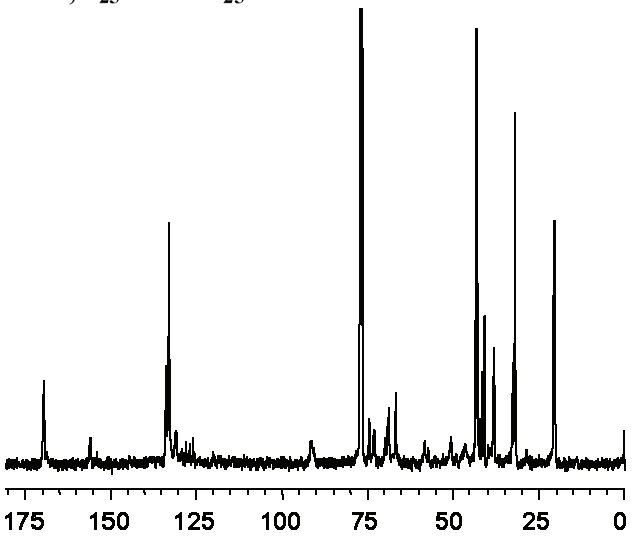
^{1}H NMR spectrum (in $CDCl_3$) for poly(3c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-ONBE



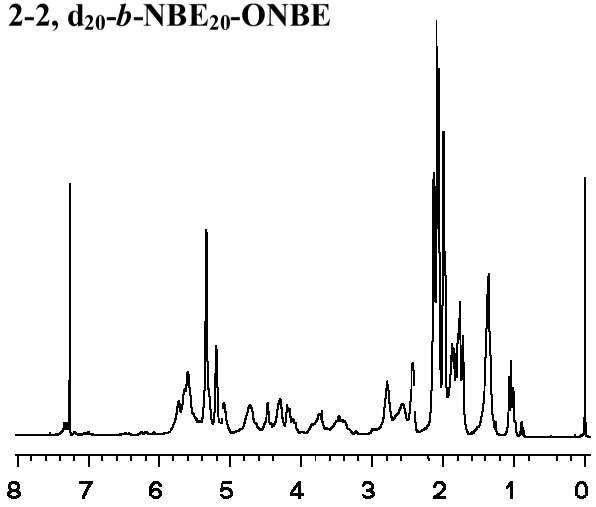
^{13}C NMR spectrum (in $CDCl_3$) for poly(3a-b), corresponding to run 8 in Table 2-1, a_{20}-*b*-b_{20}-*b*-NBE_{20}-ONBE



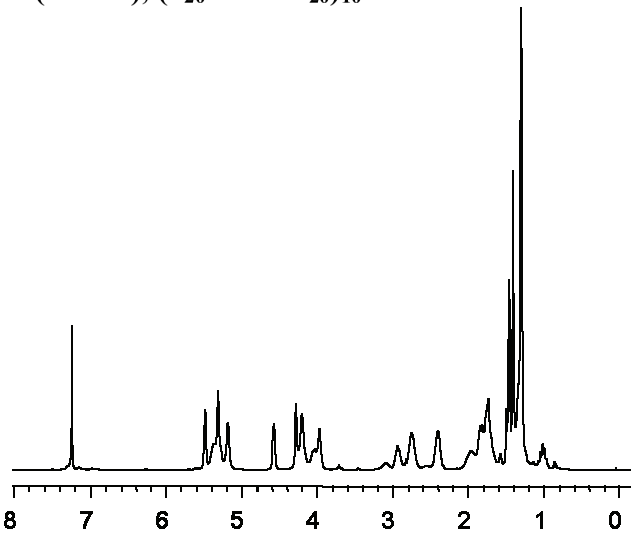
^{13}C NMR spectrum (in $CDCl_3$) for poly(3c), corresponding to run 10 in Table 2-2, c_{25}-*b*-NBE_{25}-ONBE



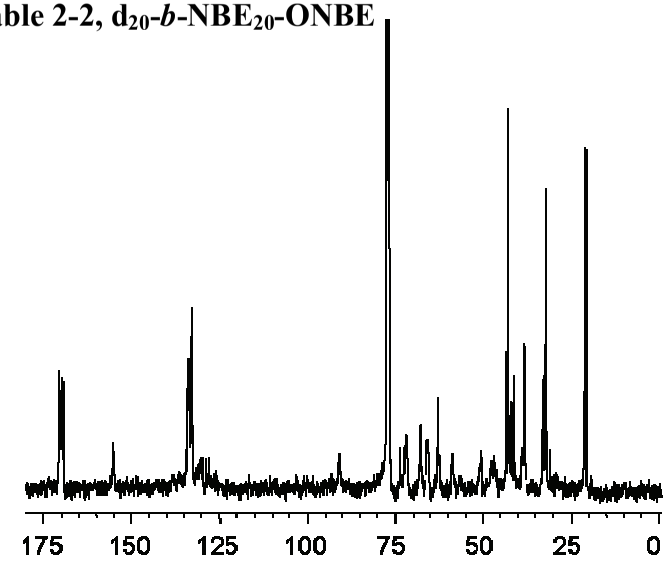
^{1}H NMR spectrum (in $CDCl_3$) for poly(3d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-ONBE



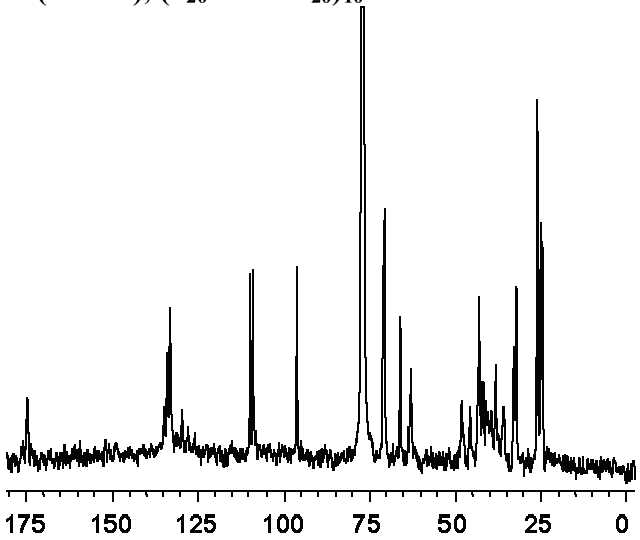
^{1}H NMR spectrum (in $CDCl_3$) for poly(4a), corresponding to run 5 in Table 1 (in text), $(a_{20}$-*b*-$NBE_{20})_{10}$



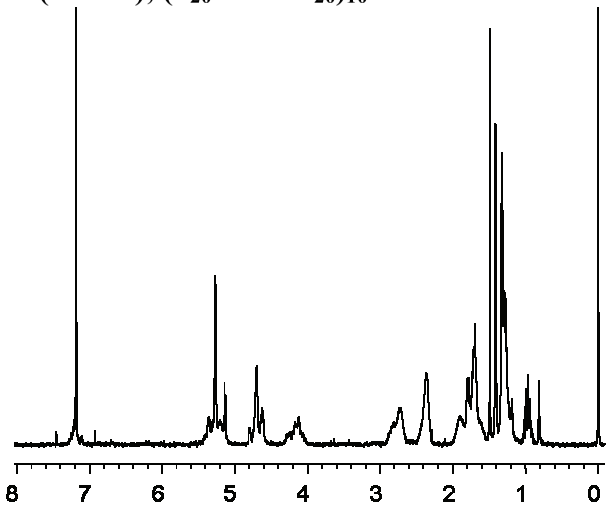
^{13}C NMR spectrum (in $CDCl_3$) for poly(3d), corresponding to run 11 in Table 2-2, d_{20}-*b*-NBE_{20}-ONBE



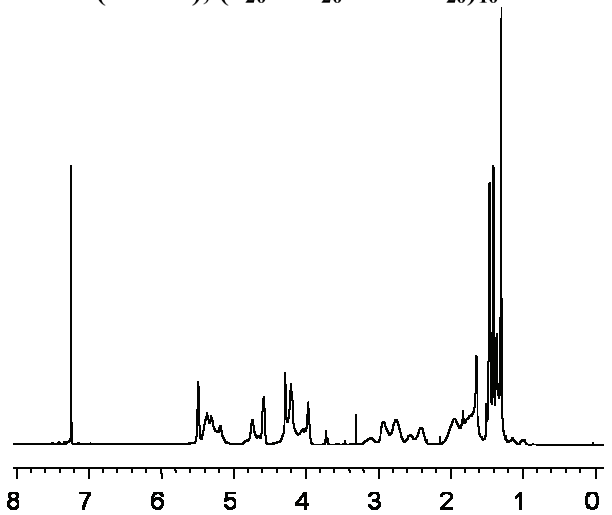
^{13}C NMR spectrum (in $CDCl_3$) for poly(4a), corresponding to run 5 in Table 1 (in text), $(a_{20}$-*b*-$NBE_{20})_{10}$



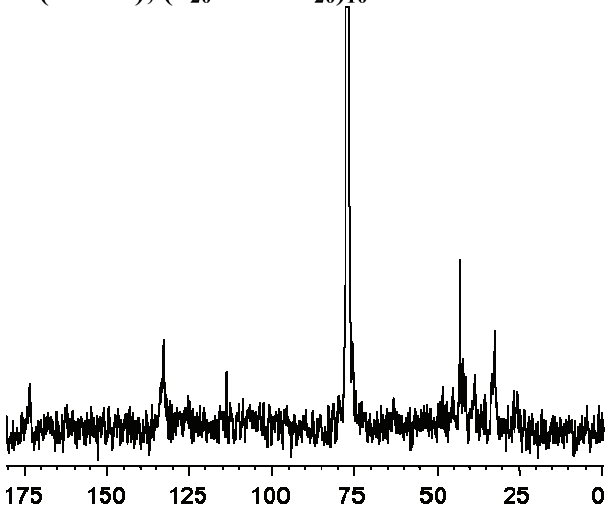
^{1}H NMR spectrum (in $CDCl_3$) for poly(4b), corresponding to run 11 in Table 1 (in text), (b_{20}-*b*-NBE_{20})$_{10}$



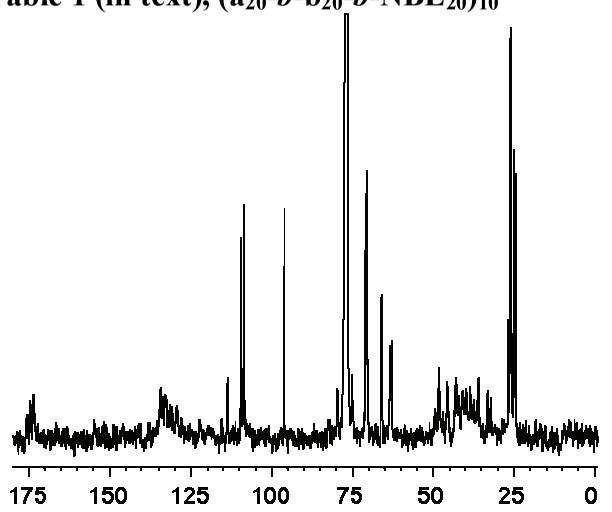
^{1}H NMR spectrum (in $CDCl_3$) for poly(4a-b), corresponding to run 12 in Table 1 (in text), (a_{20}-*b*-b_{20}-*b*-NBE_{20})$_{10}$



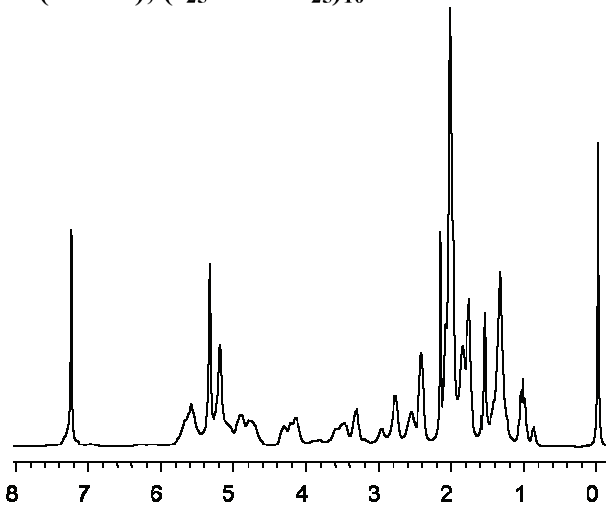
^{13}C NMR spectrum (in $CDCl_3$) for poly(4b), corresponding to run 12 in Table 1 (in text), (b_{20}-*b*-NBE_{20})$_{10}$



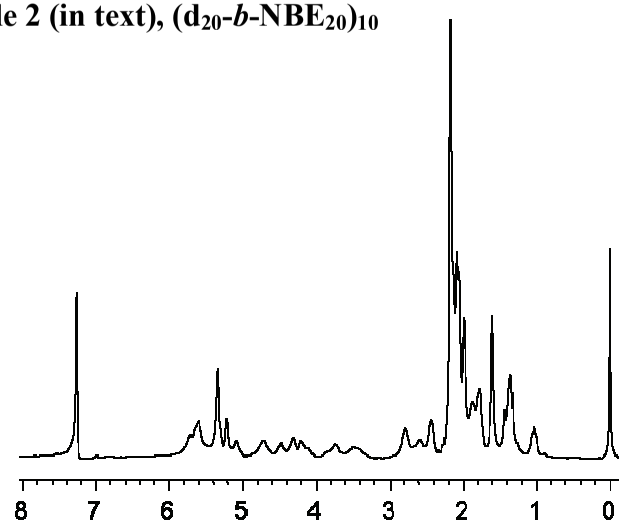
^{13}C NMR spectrum (in $CDCl_3$) for poly(4a-b), corresponding to run 12 in Table 1 (in text), (a_{20}-*b*-b_{20}-*b*-NBE_{20})$_{10}$



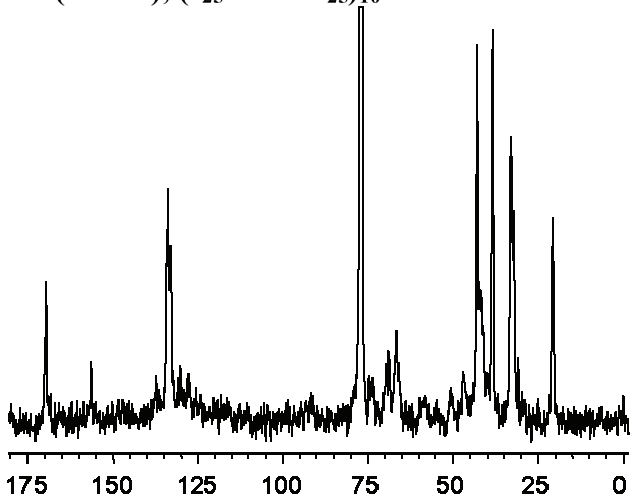
^{1}H NMR spectrum (in $CDCl_3$) for poly(4c), corresponding to run 15 in Table 2 (in text), $(c_{25}$-*b*-$NBE_{25})_{10}$



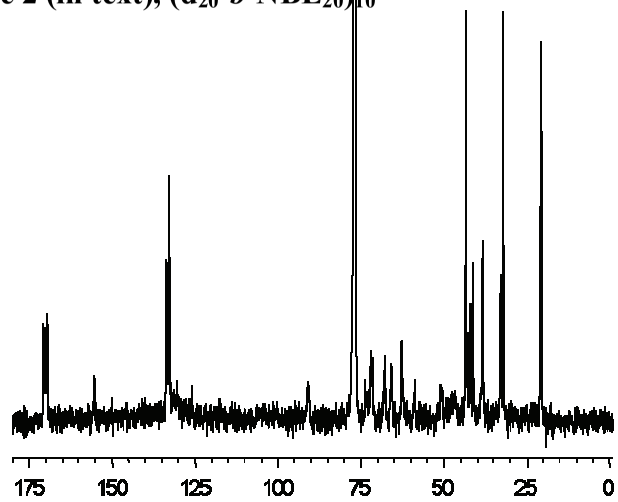
^{1}H NMR spectrum (in $CDCl_3$) for poly(4d), corresponding to run 17 in Table 2 (in text), $(d_{20}$-*b*-$NBE_{20})_{10}$



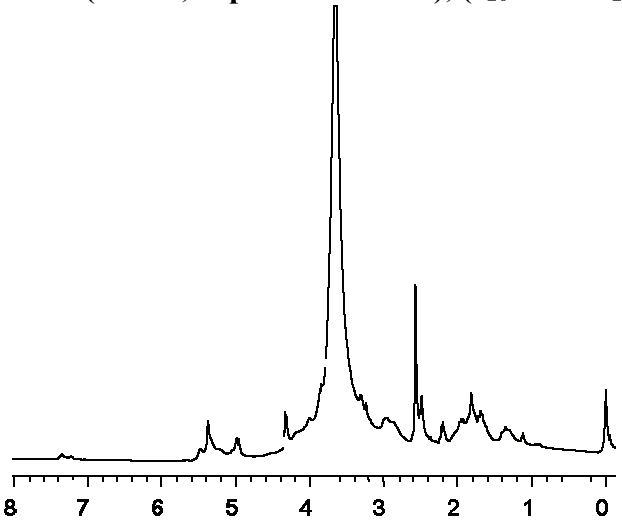
^{13}C NMR spectrum (in $CDCl_3$) for poly(4c), corresponding to run 15 in Table 2 (in text), $(c_{25}$-*b*-$NBE_{25})_{10}$



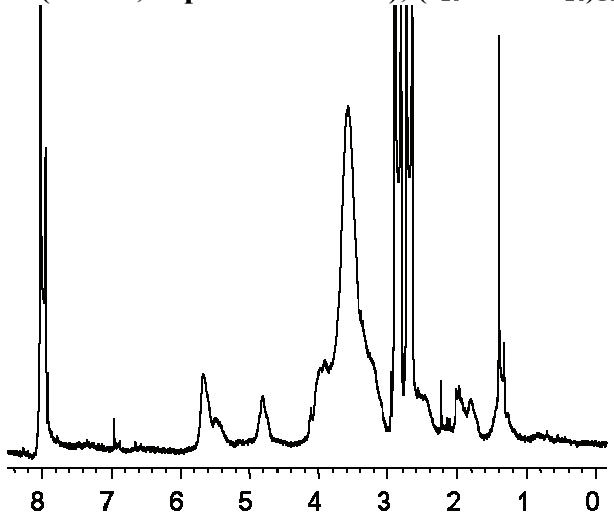
^{13}C NMR spectrum (in $CDCl_3$) for poly(4d), corresponding to run 17 in Table 2 (in text), $(d_{20}$-*b*-$NBE_{20})_{10}$



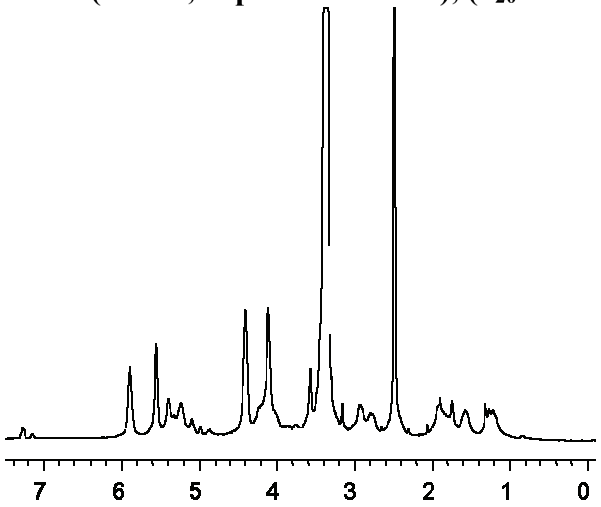
^{1}H NMR spectrum (in DMSO-d_6) for poly(5a), corresponding to run 5 in Table 1 (in text, deprotected form), (a_{20}-*b*-NBE_{20})$_{10}$



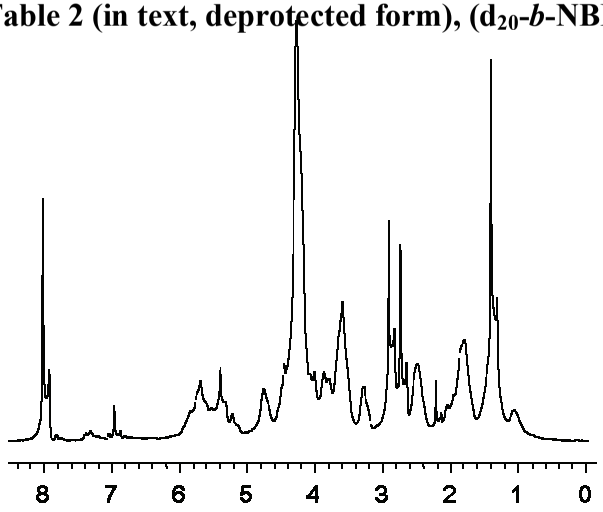
^{1}H NMR spectrum (in DMF-d_7) for poly(5c), corresponding to run 13 in Table 2 (in text, deprotected form), (c_{20}-*b*-NBE_{20})$_{10}$



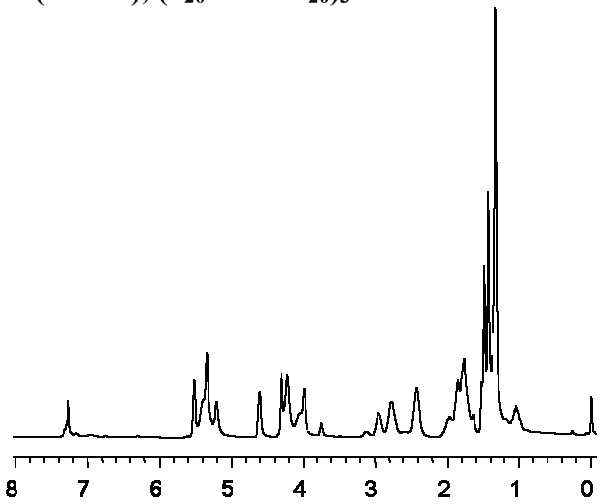
^{1}H NMR spectrum (in DMSO-d_6) for poly(5b), corresponding to run 11 in Table 1 (in text, deprotected form), (b_{20}-*b*-NBE_{20})$_{10}$



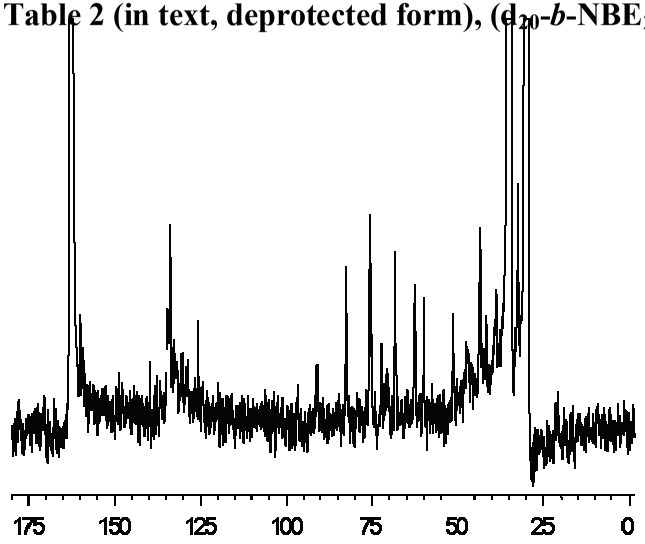
^{1}H NMR spectrum (in DMF-d_7) for poly(5d), corresponding to run 17 in Table 2 (in text, deprotected form), $(d_{20}$-*b*-$NBE_{20})_{10}$



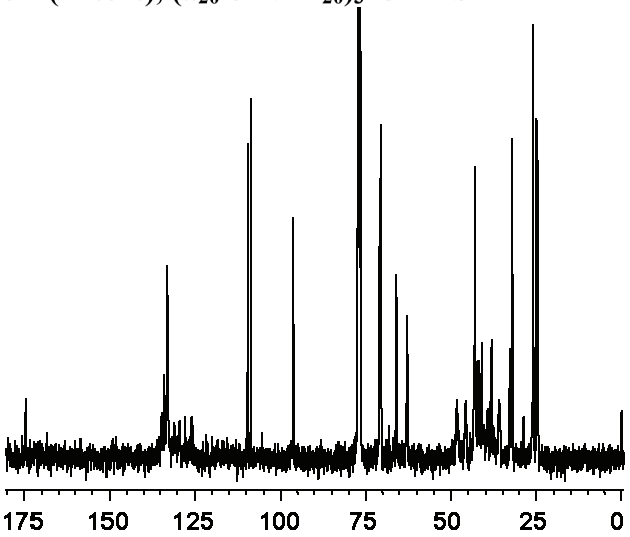
^{1}H NMR spectrum (in $CDCl_3$) for poly(6), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-OTMS



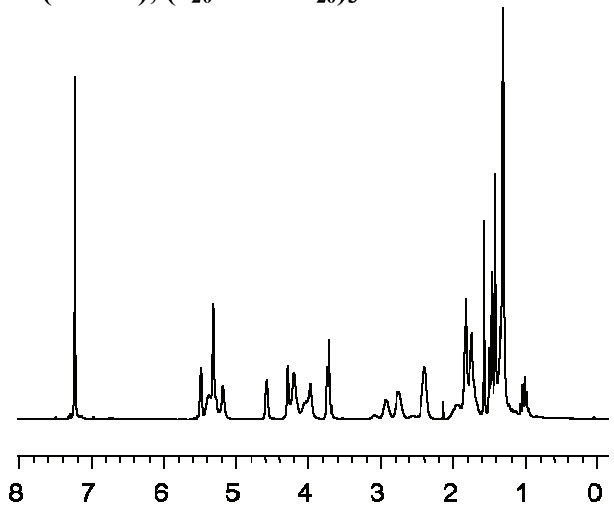
^{13}C NMR spectrum (in DMF-d_7) for poly(5d), corresponding to run 17 in Table 2 (in text, deprotected form), $(d_{20}$-*b*-$NBE_{20})_{10}$



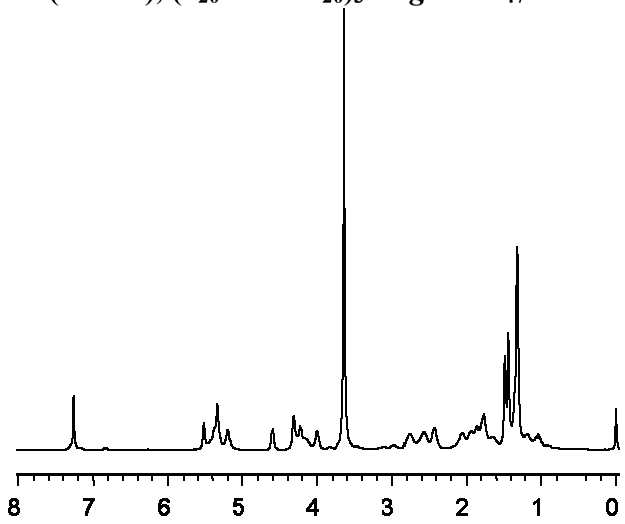
^{13}C NMR spectrum (in $CDCl_3$) for poly(6), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-OTMS



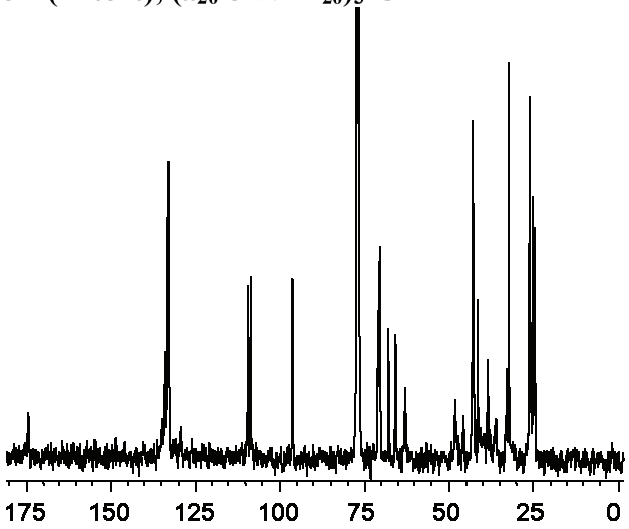
^{1}H NMR spectrum (in $CDCl_3$) for poly(7), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-OH



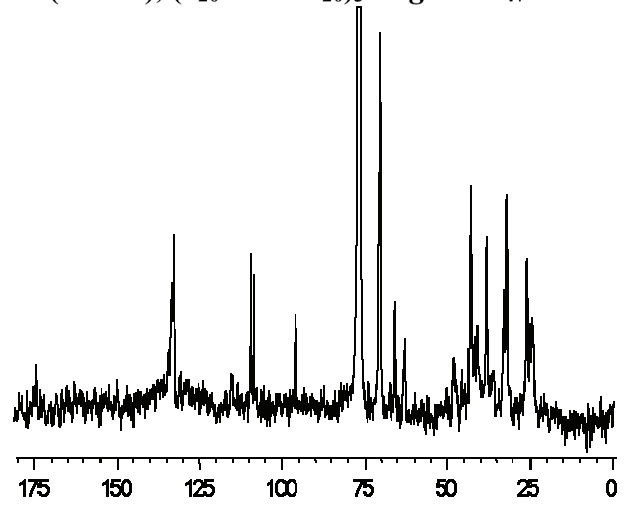
^{1}H NMR spectrum (in $CDCl_3$) for poly(8), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-O-*g*-PEG_{47}



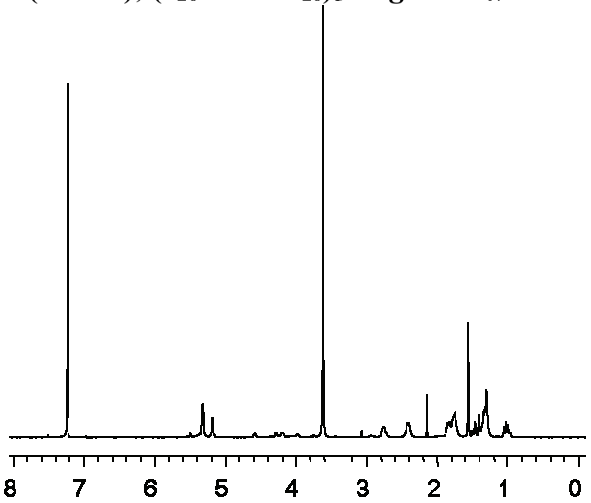
^{13}C NMR spectrum (in $CDCl_3$) for poly(7), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-OH



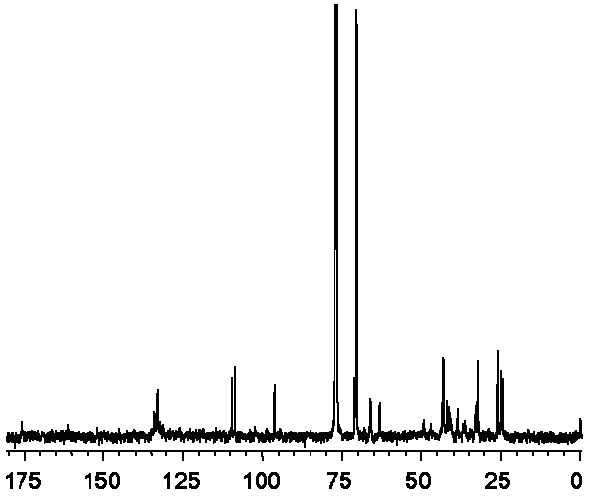
^{13}C NMR spectrum (in $CDCl_3$) for poly(8), corresponding to run 20 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_3$-O-*g*-PEG_{47}



^{1}H NMR spectrum (in $CDCl_3$) for poly(8), corresponding to run 21 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_5$-O-*g*-PEG_{47}

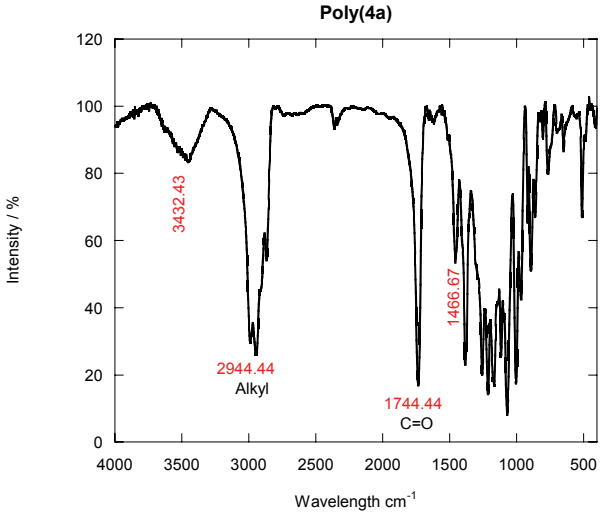


^{13}C NMR spectrum (in $CDCl_3$) for poly(8), corresponding to run 21 in Table 4 (in text), $(a_{20}$-*b*-$NBE_{20})_5$-O-*g*-PEG_{47}

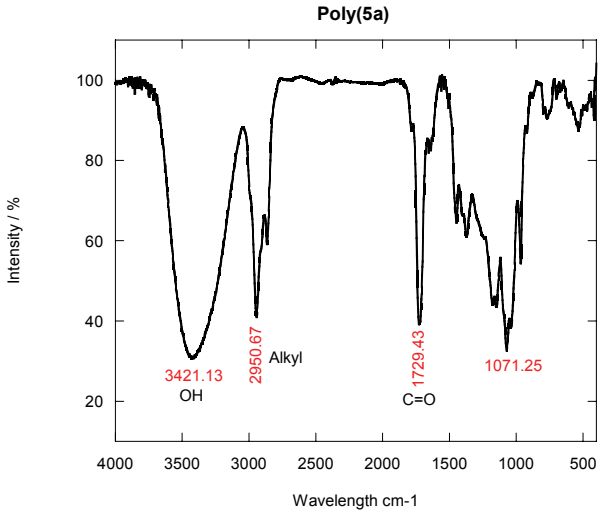


5. FT-IR spectra for poly(4a) and poly(5a).

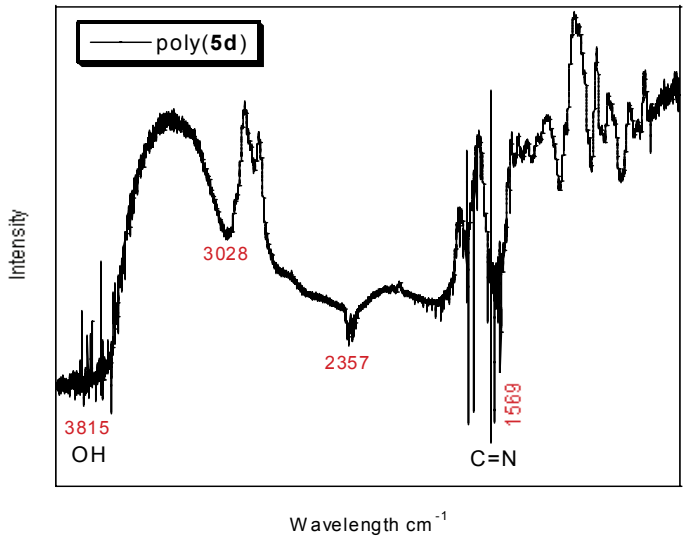
FT-IR spectrum (KBr disk) for poly(4a), [corresponding to run 4 in Table 1 (in text), (k = 10) $(NBE_{20}$-*b*-$a_{20})_{10}$



FT-IR spectrum (KBr disk) for poly(5a), [corresponding to run 4 in Table 1 (in text, deprotected form), (k = 10), $(NBE_{20}$-*b*-$a_{20})_{10}$



FT-IR spectrum (KBr disk) for poly(5d), [corresponding to run 16 in Table 2 (in text, deprotected form), (k = 10), $(NBE_{20}$-*b*-$d_{20})_{10}$



6. Measurement of spherical aggregates derived from Amphiphilic Block fragments using Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) measurements were made on thin films on an Okenshoji Co. Ltd. copper grid, which was covered with a perforated polymer film and coated with carbon on all sides (diameter 3 mm), at different concentrations of 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4} mg/mL (THF). They were then analyzed with a JEOL JEM-3100FEF electron microscope (gun type: field emission), at an accelerate voltage of 300 kV, a column vacuum of 1.0×10^{-5} Pascals (Pa), and at a magnification of 20,000×. All pictures were Energy Filtered TEM images, which were taken with an Omega energy filter for zero-loss images (cut inelastic scattered electrons). The temperature was set to 22 ^{o}C and the relative humidity was set to 50%.

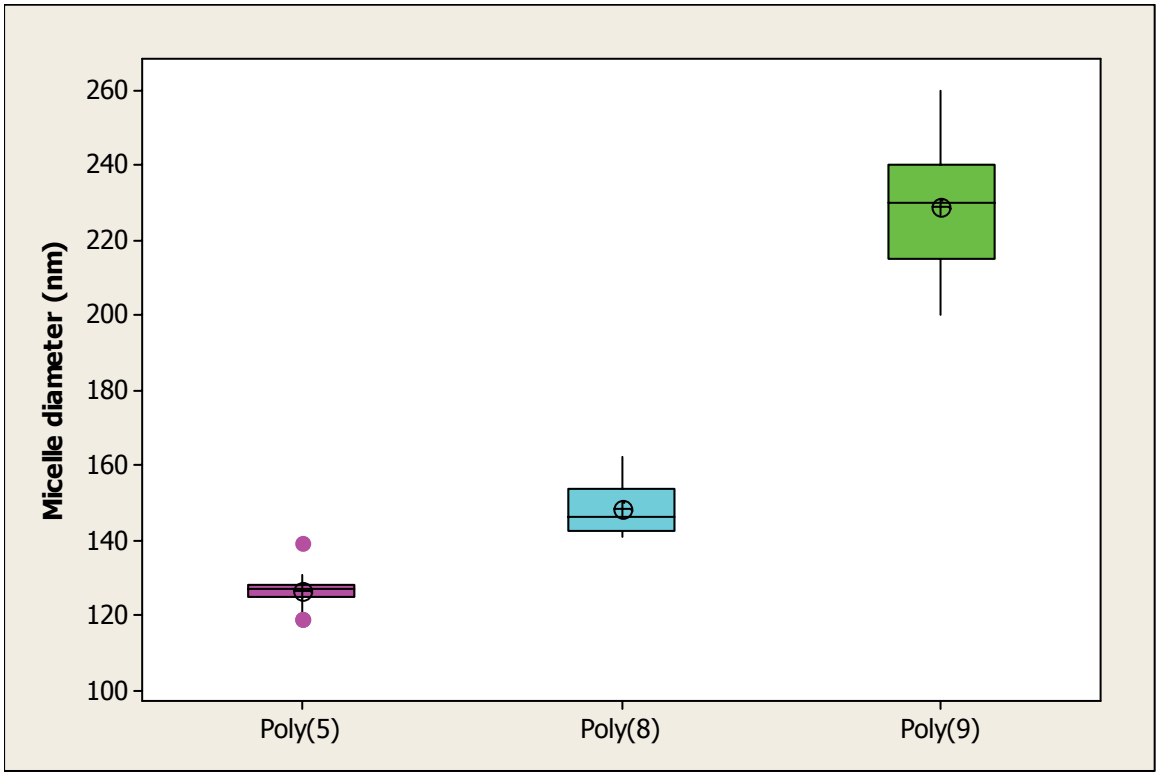
Samples for the block copolymers were first dissolved in THF to make the copolymer solution with an initial concentration of 0.05 mg/mL. Deionised water (2 mL) was added to this solution drop wise with stirring. The formation of aggregates was indicated by an increase in the viscosity of the solution. This mixture was stirred for an additional 30 minutes and then an excess of deionised water (8 mL) was added to quench the micelles. This solution was then heated at 60 ^{o}C with stirring to remove the THF and then cooled to room temperature before observation.

Supporting Information Table 6-1. Measurement of polymeric Micelles derived from amphiphilic fragments poly(**5a**), poly(**8a**) and poly(**9a**)

Run No.[a]	Micelle derived from poly(**5a**) diameter d_{TEM} (nm)	Micelle derived from poly(**8a**) diameter d_{TEM} (nm)	Micelle derived from poly(**9a**) diameter d_{TEM} (nm)
1	128.0	146.7	226.7
2	126.7	153.0	260.0
3	118.9	141.0	240.0
4	122.8	147.6	200.0
5	126.8	143.6	233.3
6	126.8	141.0	233.3
7	120.9	142.3	206.7
8	128.0	145.0	203.3
9	126.8	146.3	226.7
10	124.8	147.6	250.0
11	124.8	154.3	240.0
12	124.8	162.3	246.7
13	130.6	147.6	235.4
14	130.6	141.0	254.0
15	119.0	141.0	218.1
16	124.8	145.0	214.1
17	139.6	162.3	226.7
18	128.0	162.3	240.1
19	128.0	145.0	220.0
20	126.8	154.3	200.1
Mean	126.4	148.5	231.3
SD[b]	4.50	7.23	17.6
SEM[c]	1.01	1.62	3.94
Q1[d]	124.8	142.6	215.1
Q3[e]	128.0	154.0	240.1
Median	126.8	146.5	228.8

[a]Aggregates measured 20 times; [b]SD = Standard Deviation; [c]SEM = Standard Error of the Mean (SD/√n); [d]First Quartile: Median of lower part of data; [e]Third Quartile: Median of upper part of data.

Supporting Information Figure 6-1. Box-whisker plot[a] of the diameters of the various micelles derived from, poly(**5a**), poly(**8a**) and poly(**9a**). [⊕ = Mean Value; ● = Outlier].



[a]The box represents the subject data between the upper and lower quartiles and the whisker incorporates 95% of the data.

Supporting Information Table 6-2. Measurement of cores / shells in polymeric Micelles derived from amphiphilic fragment poly(**9a**)

Run No.	Micelle diameter d_{TEM} (nm)	Core diameter d_{TEM} (nm)	Shell diameter d_{TEM} (nm)	Core / shell ratio
1	226.7	86.7	140.0	0.62
2	260.0	106.7	153.3	0.69
3	240.0	100.0	140.0	0.71
4	200.0	86.7	113.3	0.76
5	233.3	116.7	136.7	0.85
6	233.3	100.0	133.3	0.75
7	206.7	93.3	133.3	0.82
8	203.3	106.7	126.7	0.84
9	226.7	100	126.7	0.79
10	250.0	123.3	126.7	0.97
11	240.0	120.0	120.0	1.00
12	246.7	120.0	126.7	0.95
13	235.4	126.35	109.0	1.16
14	254.0	129.0	124.9	1.03
15	218.1	107.7	110.4	0.97
16	214.1	129.0	85.1	1.52
17	226.7	93.4	133.3	0.70
18	240.1	106.7	133.4	0.80
19	220.0	100.0	120.0	0.83
20	200.1	93.4	106.7	0.88
Mean	231.3	107.3	123.9	0.88
SD[b]	17.6	13.8	15.1	0.20
SEM[c]	3.94	3.09	3.37	0.04

[a]Aggregates measured 20 times; [b]SD = Standard Deviation; [c]SEM = Standard Error of the Mean (SD/√n).

7. Preparation and encapsulation of the Hydrophobic Dye Nile Red by polymeric micelles derived from poly(5a) and poly(9a).

Procedure analogous to that described by Zhao *et al*.,[*] thus, the polymer was dissolved in THF (0.05 mg/mL) and to this was added Nile Red (0.003 mgs, 6% wt of the polymer). The bright orange-red solution was stirred to induce homogenisation after which time deionised water (2 mL) was added to form the micelle, which was indicated by an increase in viscosity and a colour change to pink. This mixture was stirred for 30 minutes and then a further 4-fold of deionised water (8 mL) was added to quench the micelles and the solution heated at 60 ^{o}C with stirring to remove the THF. The micelle/dye solution was then cooled to room temperature before observation.

Supporting Information Table 7-1. Summary of UV and Fluorescence Emission spectra from Nile Red encapsulation with poly(**5a**) and poly(**9a**)

Spectra	UV λ_{MAX} (nm)	Fluorescence Emission λ_{MAX} (nm)
Nile Red(THF)	527	590
Nile Red (THF/H_2O)	576	647
Poly(**5a**) + Nile Red (THF/H_2O)	542	639
Poly(**9a**) + Nile Red (THF / H2O)	551	650

*Jinqiang J.; Tong, X.; Zhao, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8290.

Supporting Information Figure 7-1. Preparation of Nile Red conjugated polymeric nanoparticles by addition of water to the amphiphilic poly(macromonomer) poly(**5a**), $(NBE_{20}$-*b*-$\mathbf{a}_{20})_{10}$ solution in THF (0.05 mg/mL)