

Supplementary Information (ESI) for Chemical Communications

Precise Synthesis of Poly(macromonomer)s Containing Sugars by Repetitive Ring-Opening Metathesis Polymerisation (ROMP)

James J. Murphy and Kotohiro Nomura*

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST),

8916-5 Takayama, Ikoma, Nara 630-0101, Japan; E-mail: nomurak@ms.naist.jp

Contents

1. Experimental procedures for the preparation of diblock copolymers poly(**1**), end group deprotected copolymers poly(**2**), macromonomers poly(**3**), poly(macromonomer)s poly(**4**) and deprotected poly(macromonomer)s poly(**5**).
2. GPC traces for macromonomer and poly(macromonomer)s
3. ^1H and ^{13}C NMR spectra for poly(**1**) - poly(**5**).
4. FT-IR spectra for protected poly(macromonomer) poly(**4a**) and deprotected poly(macromonomer) poly(**5a**).

1. Experimental procedures

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres dry-box or using standard Schlenk techniques. 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 dry-box, 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 dry-box. The molybdenum initiators of the type (ArN)Mo(CHCMe₂Ph)(OR)₂ [Ar = 2,6-*i*-Pr₂C₆H₃, R = ^tBu (**A1**) or CMe(CF₃)₂ (**A2**); Ar = 2,6-Me₂C₆H₃, R = CMe(CF₃)₂ (**A3**)],¹ and 5-norbornene carboxylic acid chloride² were prepared according to the literature, and Ru(CHPh)(Cl)₂(ImesH₂)(PCy₃) (**B**, ImesH₂ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), was purchased from Strem Chemicals, Inc. and used without further purification. Polymerisation grade of 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranos-6-*O*-yl 5-norbornene-2-carboxylate (**a**), ribonic- γ -lactone-norbornene-2-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 report³. 4-Me₃Si-C₆H₄CHO was also prepared according to the previous report.⁴

All ¹H- and ¹³C-NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (¹H, 399.65 MHz; ¹³C, 100.40 MHz), and were obtained in the solvent indicated at 25 °C, with all chemical shifts quoted in ppm and referenced to SiMe₄. HPLC grade THF was used for GPC and was degassed prior to use. GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu 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 x 8.0 mm ϕ) were calibrated versus polystyrene standard samples.

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.^{3,5} Synthetic procedure for poly(**1a**) was according to our previous report.⁵ A toluene solution of Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)(O^tBu)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 added in one portion and the reaction mixture stirred for the additional required time. The polymerisation was quenched by adding 4-trimethylsilyloxybenzaldehyde (~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%; ¹H NMR (CDCl₃) δ = 7.51 (s), 6.97 (s), 5.58 (br), 5.39 (br) (11H, olefinic and aromatic end group protons), 5.37-5.18 (4H, br, HC=CH), 5.49 (br s), 4.58 (br s), 4.29-4.21 (br d), 3.97 (br s) (7H, sugar group protons), 2.93 (br), 2.75 (br), 2.40 (br), 1.95-1.74 (br) (15H, protons of five-membered ring), 1.54 (br s), 1.46 (br s), 1.41 (br s), 1.34 (br s), 1.31 (br s) (12H, 4xCH₃), 0.24 (9H, s, Si(CH₃)₃); ¹³C NMR (CDCl₃) δ = 174.4 (C=O), 133.8-132.8 (C=C), 109.5, 108.7 (2xCM₂), 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 (4xCH₃). As reported previously,^{3,5} the resultant ring-opened polymer, poly(**1a**), possessed a mixture of *cis* and *trans* olefinic double bonds and the polymer by polymerization of **a** probably possessed a mixture of head-to-head, head-to-tail and tail-to-tail arrangement of the repeat unit.

Poly(1b): Synthesis of block copolymers of norbornene (NBE) and ribonic- γ -lactone-norbornene-2-carboxylate. Preparation analogous to that described above afforded poly(**1b**) as white precipitates. Yield = 96-98%; ¹H NMR (CDCl₃) δ = 7.51 (s), 6.97 (s), 5.58

(br), (11H, olefinic and aromatic end group protons), 5.39-5.16 (4H, br, HC=CH), 5.49 (br m), 4.74-4.67 (br m), 4.29-4.10 (br m) (5H, sugar group protons), 2.86-2.76 (br d), 2.41 (br s), 1.94-1.67 (br m) (15H, protons of five-membered ring), 1.45 (br s), 1.36 (br s), 1.35 (br s), 1.34 (br s) (6H, 2×CH₃), 0.22 (9H, s, Si(CH₃)₃); ¹³C NMR (CDCl₃) δ = 175.4, 175.2 (C=O), 135.6, 134.9, 134.7 (C=C), 114.4 (CMe₂), 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×CH₃), 1.9 (Si(CH₃)₃). As reported previously,^{3,5} the resultant ring-opened polymer, poly(**1b**), possessed a mixture of *cis* and *trans* olefinic double bonds and the polymer by polymerization of **b** 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.⁵ The synthetic procedure for poly(**2a**) by hydrolysis of TMS group was according to the previous report.⁵ 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 (CDCl₃) δ = 7.51 (s), 6.97 (s), 5.58 (br), 5.39 (br) (11H, olefinic and aromatic end group protons), 5.37-5.17 (4H, br, HC=CH), 5.49 (br s), 4.58 (br s), 4.28-4.20 (br d), 3.97 (br) (7H, sugar group protons), 2.93-2.76 (br d), 2.40 (br s), 1.86-1.74 (br) (15H, protons of five-membered ring), 1.47 (br s), 1.41 (br s), 1.34 (br s), 1.30 (br s) (12H, 4×CH₃); ¹³C NMR (CDCl₃) δ = 174.6 (C=O), 134.6-129.3 (C=C), 109.5, 108.7 (2×CMe₂), 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 ring), 26.0, 25.6, 25.0, 24.5 (4×CH₃).

Poly(2b): Removal of TMS protection from copolymer terminus. Procedure analogous to that described above afforded poly(**2b**). Yield = 98-99%; ¹H NMR (CDCl₃) δ = 7.51 (s), 6.97 (s), 5.58 (br) (11H, olefinic and aromatic end group protons), 5.32-5.17 (4H, br, HC=CH),

5.39 (br m), 4.82-4.67 (br m), 4.29-4.16 (br m) (5H, sugar group protons), 2.79-2.76 (br d), 2.39 (br s), 1.94-1.70 (br m) (15H, protons of five-membered ring), 1.46 (br s), 1.37 (br s), 1.35 (br s), 1.34 (br s) (6H, 2×CH₃); ¹³C NMR (CDCl₃) 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 (CMe₂), 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 ring), 26.7, 25.8, 25.6 (2×CH₃).

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.⁴ The deprotected polymer, poly(2a), and Et₃N (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 dry-box. Yield = 98-99%; ¹H NMR (CDCl₃) δ = 7.29-7.19 (m) (11H, protons from aromatic and olefinic end groups), 6.87 (d), 6.27 (d), 6.04 (m) (2H, NBE olefinic protons), 5.37-5.17 (4H, br, polymer olefinic protons), 5.49 (br s), 4.58 (br s), 4.28-4.02 (br d), 3.96 (br s) (7H, sugar group protons), 3.78 (br s), 3.51 (m), 3.38 (m) (7H, NBE non-olefinic protons), 3.09 (br), 2.92 (br), 2.75 (br), 2.39 (br), 1.94-1.21 (m) (15H, protons of five membered ring), 1.01 (br s), 0.98 (br s), 0.96 (br s) (12H, 4×CH₃); ¹³C NMR (CDCl₃) 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×CMe₂), 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×CH₃).

Poly(3b): Preparation of macromonomer. Preparation analogous to that described above afforded the macromonomer, poly(**3b**), as white precipitates. Yield = 98-99%; ¹H NMR (CDCl₃) δ = 7.29-7.19 (m) (aromatic and olefinic end group protons), 6.31 (d), 6.26-6.22 (d), 6.03 (m) (2H, NBE olefinic protons), 5.40 (br s), 5.35 (br s), 5.31-5.30 (br m), 5.18-5.16 (br d) (4H, polymer olefinic protons), 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) (5H, sugar group protons), 3.74-3.59 (7H, m, NBE non olefinic protons), 3.18-2.76 (br m), 2.39 (br s), 1.94 (br), 1.86-1.69 (br m) (15H, protons from five membered rings), 1.43 (s Me), 1.35 (br s), 1.33 (br s), 1.32 (br s) (6H, 2×CH₃); ¹³C NMR (CDCl₃) 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 (CMe₂), 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×CH₃).

Poly(4a): Preparation of poly(macromonomer). The typical procedure is as follows: Poly(**3a**) (80 mg, 10 equivs. to the initiator **A3**) was dissolved in toluene (2.0 g), and Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₄)[OCMe(CF₃)₂]₂ (**A3**) in toluene (0.5 g) was added in one portion at room temperature. The mixture was stirred for the prescribed time, and the polymerisation was terminated by the addition of benzaldehyde in excess amount. The solution was stirred for 1 hour to ensure completion, and then was poured into cold methanol to isolate the product, poly(**4a**) as white precipitates. Yield = 96-98%; ¹H NMR (CDCl₃) δ = 7.50 (s), 7.29 (s), 7.16 (s), 7.14 (s), 6.97 (s), 6.93 (br) (11H, aromatic and olefinic end group protons), 5.32-5.19 (4H, br, HC=CH), 5.49 (br s), 4.58 (br s), 4.29-4.20 (br d), 3.97 (br) (7H, sugar group protons), 3.10-2.93 (br d), 2.76 (s), 2.40 (br s), 1.95-1.74 (br) (15H, protons of five-membered rings), 1.47 (br s), 1.41 (br s), 1.32 (br s), 1.30 (br s) (12H, 4×CH₃); ¹³C NMR

(CDCl₃) δ = 174.4 (C=O), 134.8, 134.6, 133.9, 133.6-132.7, 129.5 (C=C), 109.5, 108.7 (2×CMe₂), 96.2, 76.7, 71.0-70.4, 65.8, 62.9 (sugar group), 45.7, 43.4-41.4, 38.6, 36.1, 32.9-32.2 (five-membered rings), 26.0, 25.0, 24.5 (4×CH₃); FT-IR (KBr disc) 1744 cm⁻¹ (br s, C=O).

Poly(4b): Preparation of poly(macromonomer). Preparation analogous to that described above afforded the product, poly(4b), as white precipitates. Yield = 95-96%; ¹H NMR (CDCl₃) δ = 7.45 (s), 7.26 (s), 7.16 (s), 7.11 (s), 6.93 (s), 6.70 (br) (11H, aromatic and olefinic end group protons), 5.36 (m), 5.31 (m), 5.29-5.20 (m), 5.14-5.13 (br d) (4H, HC=CH), 5.53 (br s), 4.79 (br s), 4.70-4.63 (br d), 4.29-4.01 (br m) (5H, sugar group protons), 2.81-2.72 (br m), 2.39 (br s), 2.35 (br s), 1.92-1.71 (br) (15H, protons of five-membered rings), 1.49 (br s), 1.41 (br s), 1.32 (br s), 1.30 (br s) (6H, 2×CH₃); ¹³C NMR (CDCl₃) δ = 174.3, 173.6, 172.9 (C=O), 132.9, 132.1, 131.7, 130.4, 128.6, 125.5 (C=C), 113.7, 108.9 (CMe₂), 100.7, 92.9, 81.3, 79.7, 75.4, 63.0 (sugar group), 49.2, 48.5, 47.0, 45.1, 43.1-41.4, 38.3, 36.6, 35.5, 32.2 (five-membered rings), 26.9, 25.7, 25.4 (2×CH₃); FT-IR (KBr disc) 1746 cm⁻¹ (br s, C=O).

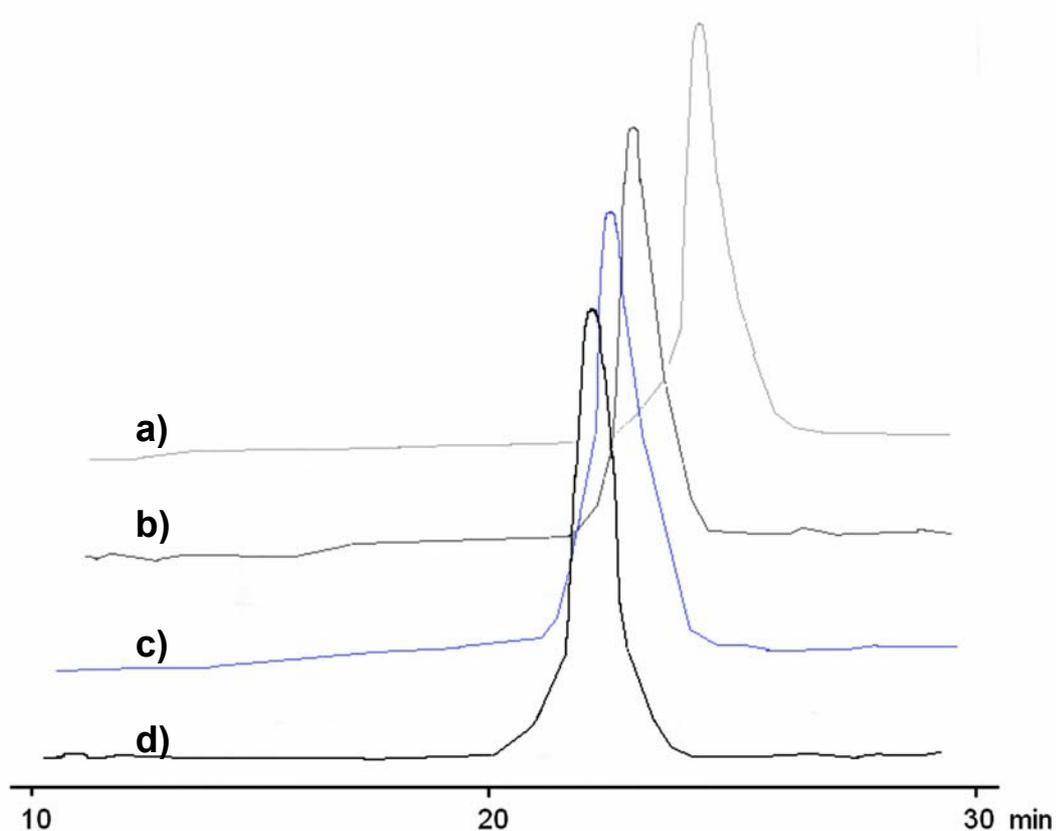
Poly(5a): Hydrolysis of diisopropylidene groups from poly(4a). The general method of acetal deprotection was as follows:^{3,5} poly(4a) was added to a solution consisting of CF₃CO₂H/H₂O (9/1, v/v, 1.5 g), and the reaction stirred at room temperature for 15 minutes. The homogeneous pale blue solution was then poured dropwise into a vigorously stirred THF solution (~70 mL) at 0 °C. The pale to white precipitates were collected by filtration, washed with THF, hexane and ether and then dried *in vacuo* to afford the deprotected poly(macromonomer), poly(5a) as a white solid. Yield = 91 %; ¹H NMR (DMSO-*d*₆) δ = 7.38-7.10 (br d) (9H, aromatic end group protons), 5.48-5.23 (4H, br, HC=CH), 4.98 (br), 4.33 (br), 4.17 (br), 4.00 (br), 3.86 (br) (11H, sugar group protons), 2.97 (br), 2.57-2.36 (br d), 2.24 (br), 1.97 (br), 1.49 (br), 1.36 (br) (15H, protons of five membered rings); FT-IR (KBr disc) 3421 (br, OH), 1729 cm⁻¹ (br s, C=O).

Poly(5b): Hydrolysis of diisopropylidene groups from poly(4b). Preparation analogous to that described above afforded poly(5b) as white precipitates. Yield = 86%; ¹H NMR (DMSO-*d*₆) δ = 7.27 (br d), 7.14 (br s) (9H, aromatic end group protons), 5.89 (br s), 5.40-5.34 (br d), 5.11, 4.99, 4.89 (m) (4H, HC=CH), 5.55 (br s), 4.40-4.11 (br d), 3.58, 3.16 (m), 2.93-2.79 (br d) (7H, sugar group protons), 2.07-1.57 (br m), 1.32-1.22 (br m) (15H, protons of five membered rings); FT-IR (KBr disc) 3417 (br, OH), 1724 cm⁻¹ (br s, C=O).

References

- 1 (a) G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Reagan, J.K. Thomas, W.M. Davis, *J. Am. Chem. Soc.*, 1990, **112**, 8378-8387; (b) G.C. Bazan, J.H. Oskam, H. Cho, L.Y. Park, R.R. Schrock, *J. Am. Chem. Soc.*, 1991, **113**, 6899-6907.
- 2 (a) Z. Koniya, C. Pugh, R.R. Schrock, *Macromolecules*, 1992, **25**, 6586-6592; (b) F. Sinner, M. R. Buchmeiser, R. Tessadri, M. Mupa, K. Wurst, K. Bonn, *J. Am. Chem. Soc.*, 1998, **120**, 2790-2797.
- 3 K. Nomura, R. R. Schrock, *Macromolecules*, 1996, **29**, 540-545.
- 4 K. Nomura, S. Takahashi, Y. Imanishi, *Macromolecules*, 2001, **34**, 4712-4723.
- 5 J. J. Murphy, T. Kawasaki, M. Fujiki, K. Nomura, *Macromolecules*, 2005, **38**, 1075-1083.

2. GPC traces for macromonomer and poly(macromonomer)s



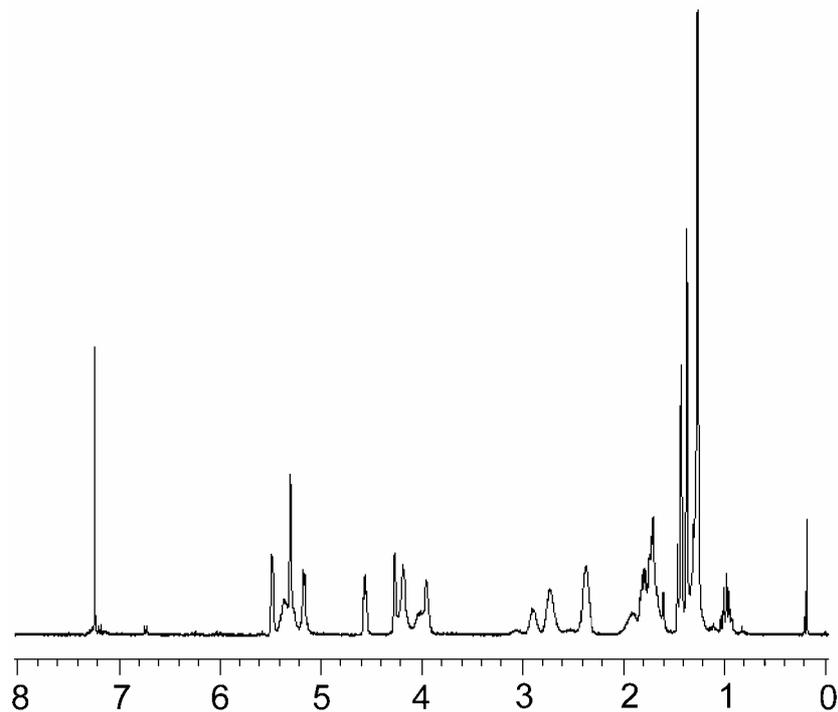
a) Macromonomer; $M_n = 1.28 \times 10^4$; $M_w/M_n = 1.11$; run 1

b) Poly(macromonomer); $M_n = 3.99 \times 10^4$; $M_w/M_n = 1.19$; $DP_n = 3.1$; run 12

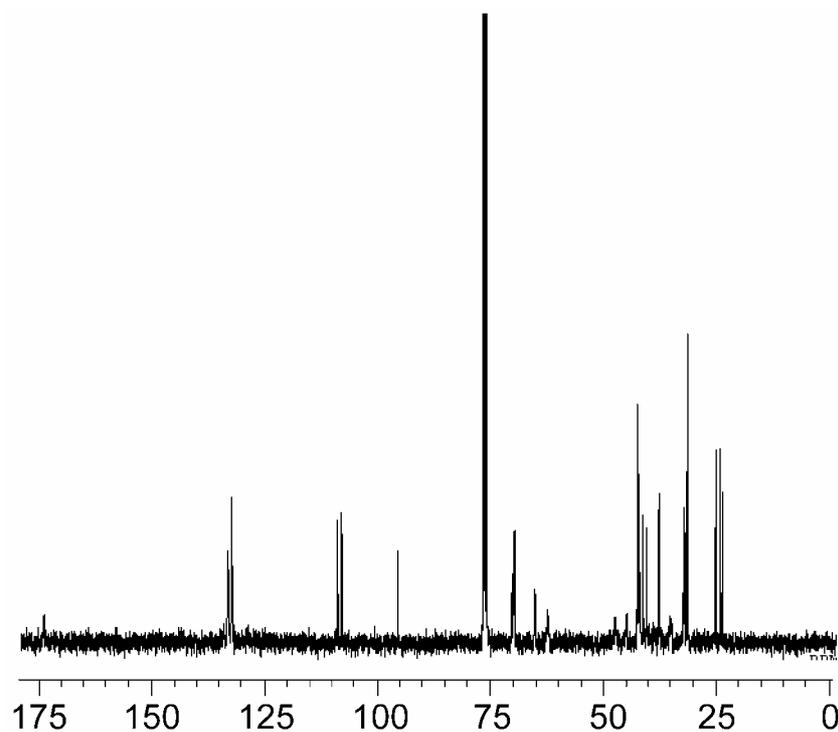
c) Poly(macromonomer); $M_n = 5.87 \times 10^4$; $M_w/M_n = 1.09$; $DP_n = 4.6$; run 11

d) Poly(macromonomer); $M_n = 11.76 \times 10^4$; $M_w/M_n = 1.07$; $DP_n = 9.2$; run 10

3. ^1H NMR spectrum (in CDCl_3) for poly(1a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].

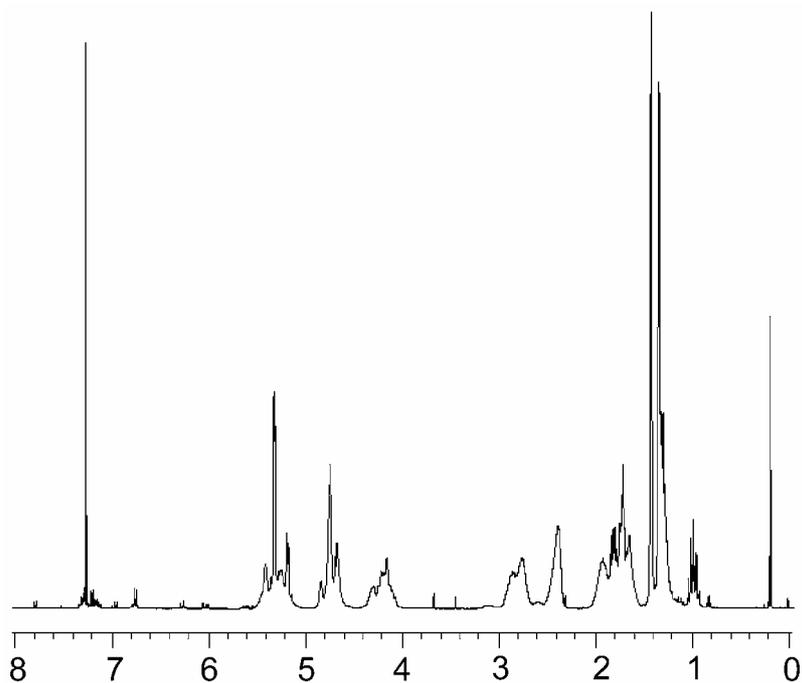


^{13}C NMR spectrum (in CDCl_3) for poly(1a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].

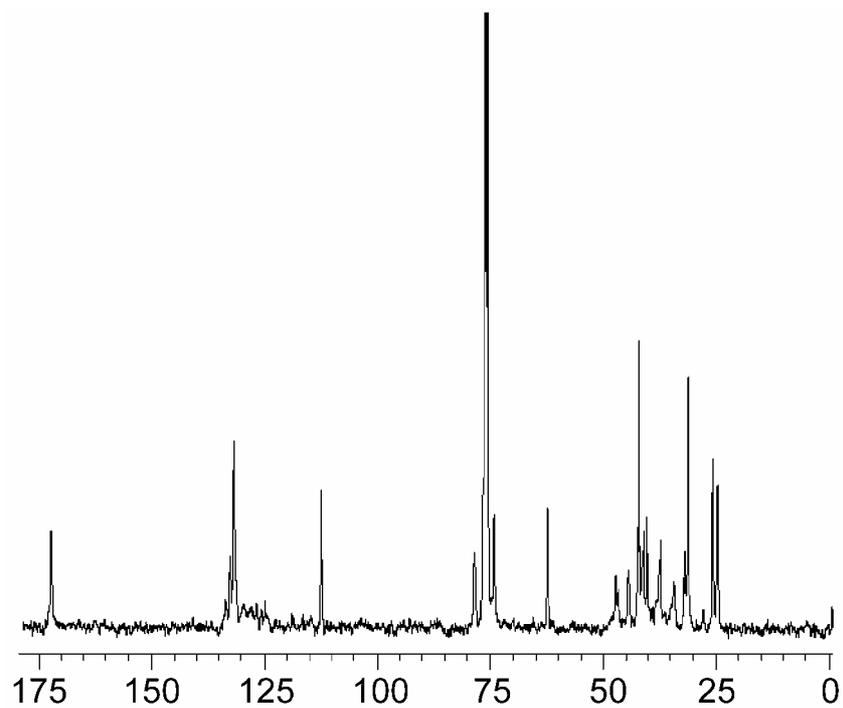


Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

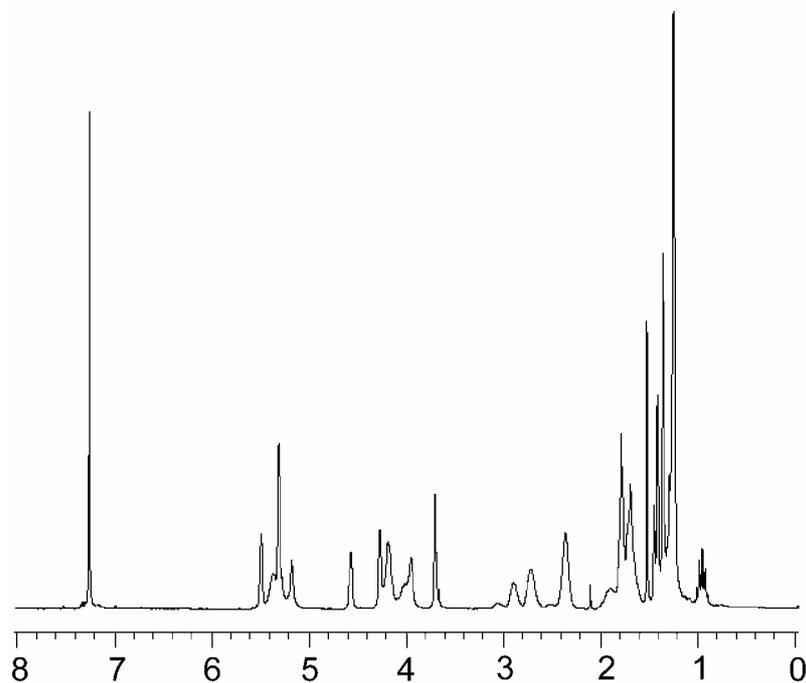
¹H NMR spectrum (in CDCl₃) for poly(1b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



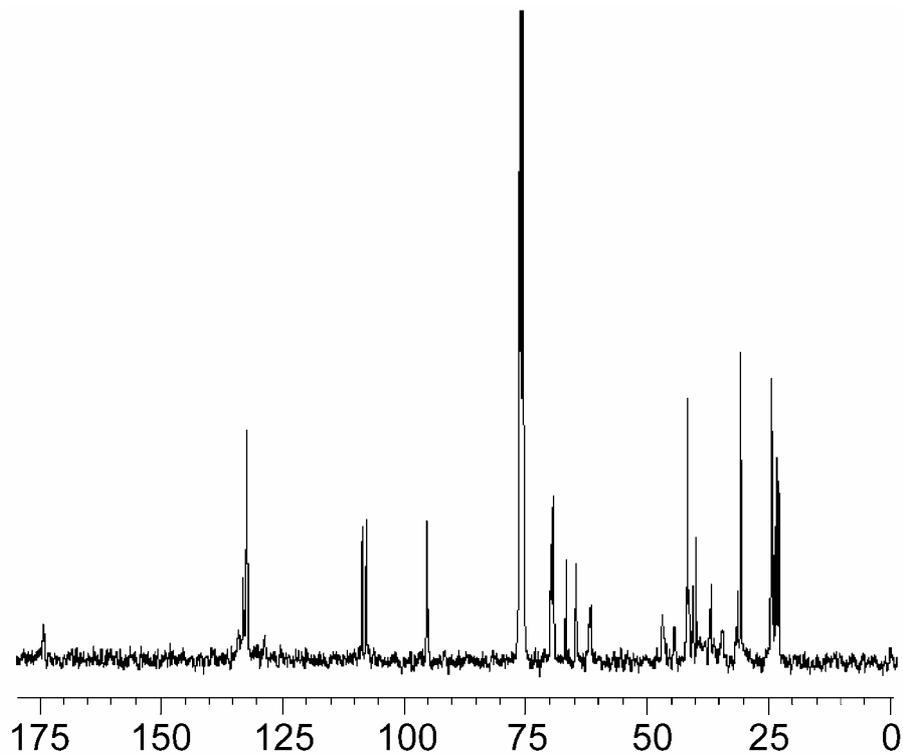
¹³C NMR spectrum (in CDCl₃) for poly(1b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



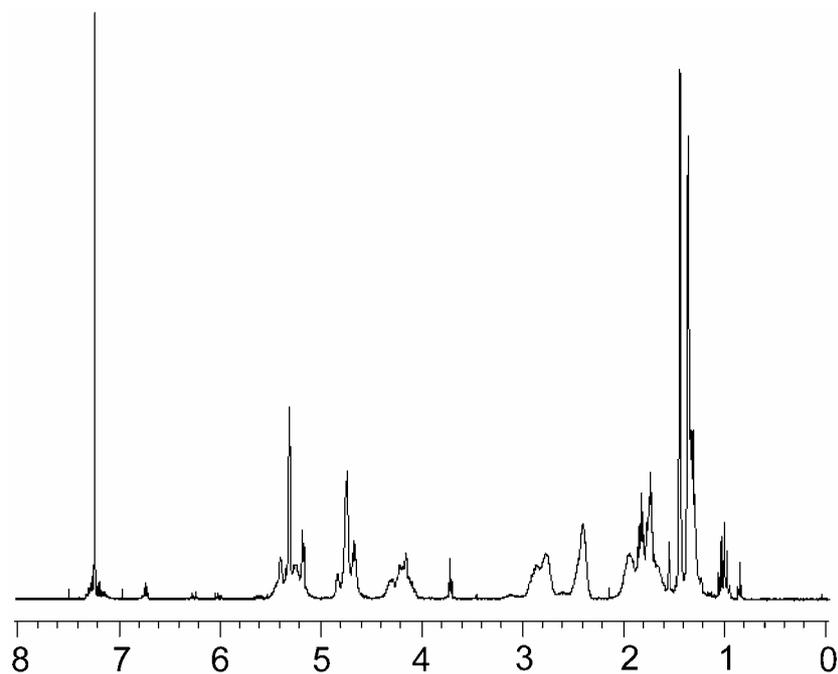
¹H NMR spectrum (in CDCl₃) for poly(2a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].



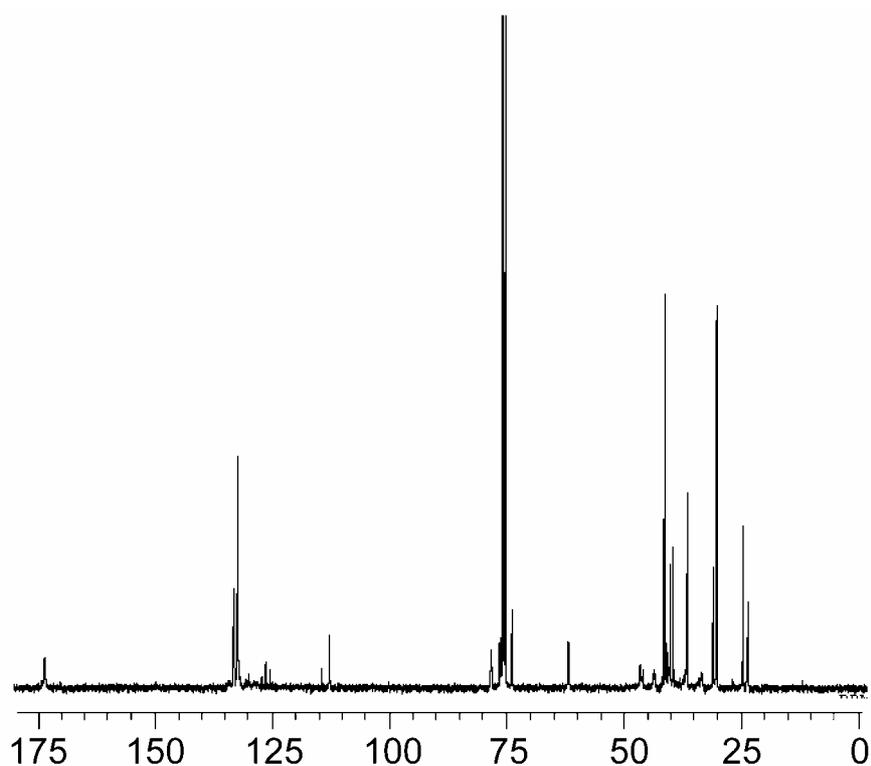
¹³C NMR spectrum (in CDCl₃) for poly(2a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].



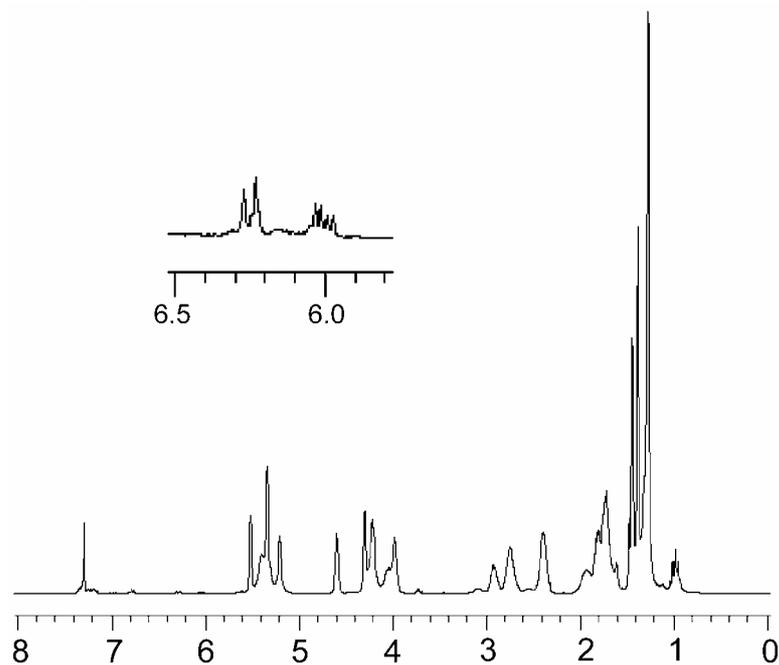
¹H NMR spectrum (in CDCl₃) for poly(2b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



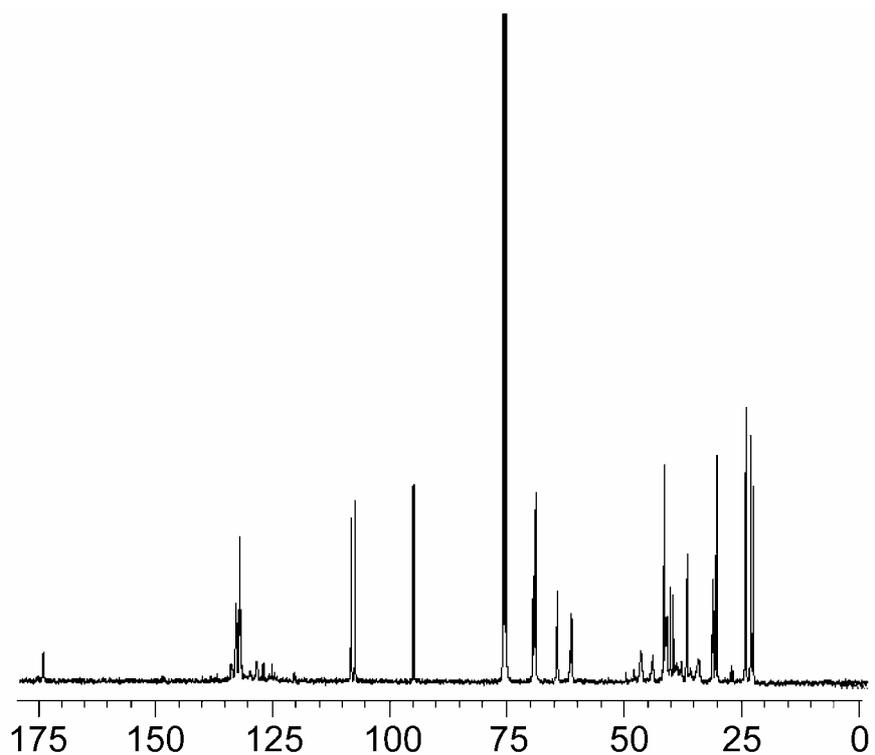
¹³C NMR spectrum (in CDCl₃) for poly(2b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



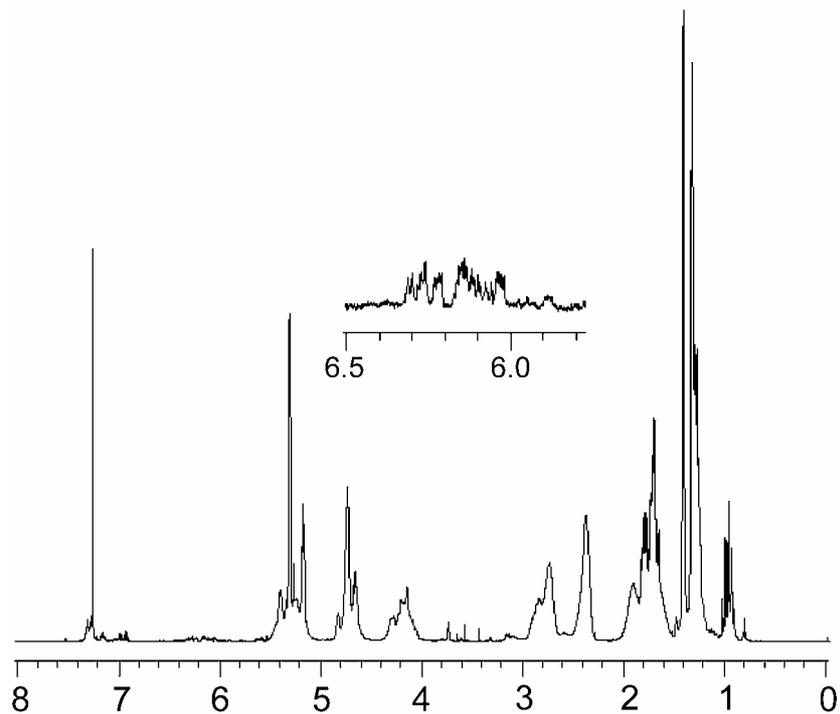
¹H NMR spectrum (in CDCl₃) for poly(3a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].



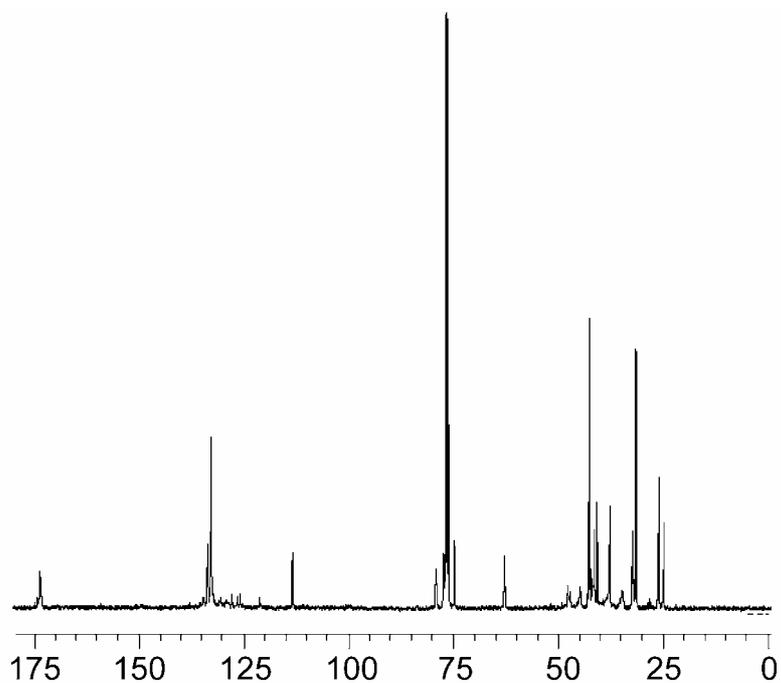
¹³C NMR spectrum (in CDCl₃) for poly(3a), corresponding to run 1 in Table 1, poly[(a)₂₀-*bl*-(NBE)₂₀].



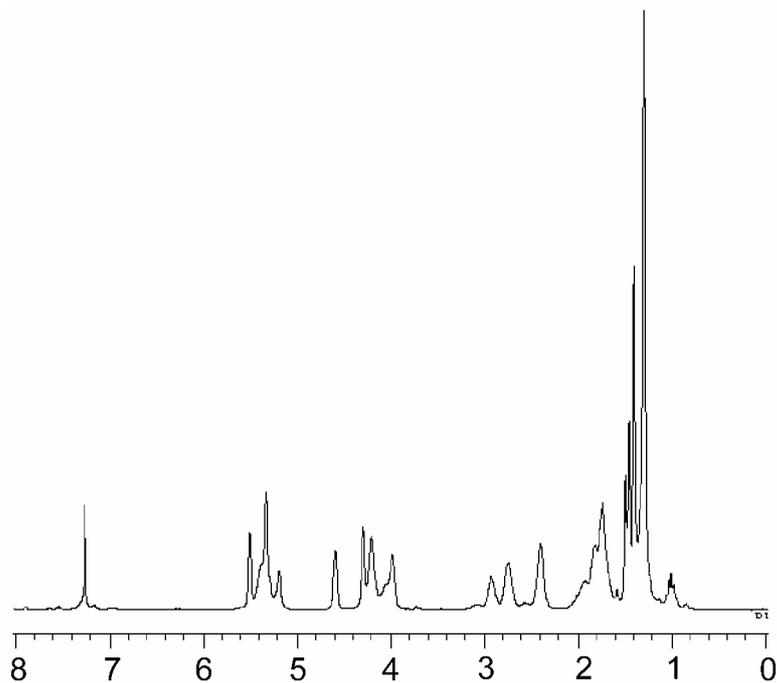
¹H NMR spectrum (in CDCl₃) for poly(3b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



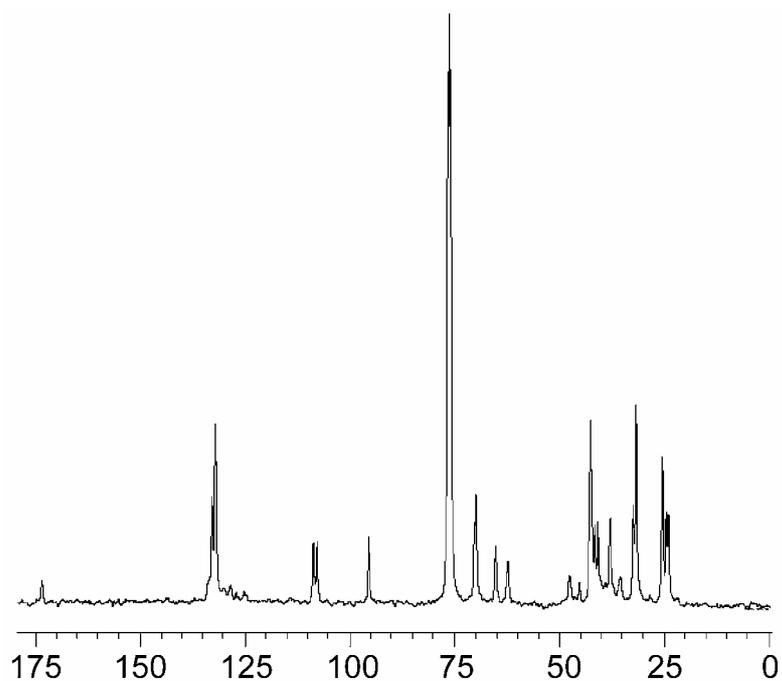
¹³C NMR spectrum (in CDCl₃) for poly(3b), corresponding to run 5 in Table 1, poly[(b)₂₀-*bl*-(NBE)₂₀].



¹H NMR spectrum (in CDCl₃) for poly(macromonomer), poly(4a), corresponding to run 12 in Table 2, (k = 3).

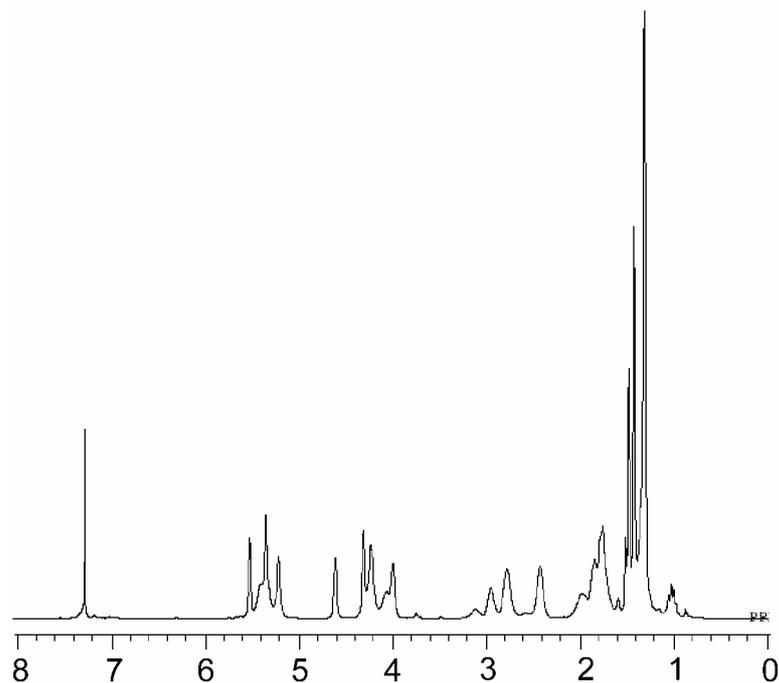


¹³C NMR spectrum (in CDCl₃) for poly(macromonomer), poly(4a), corresponding to run 12 in Table 2, (k = 3).

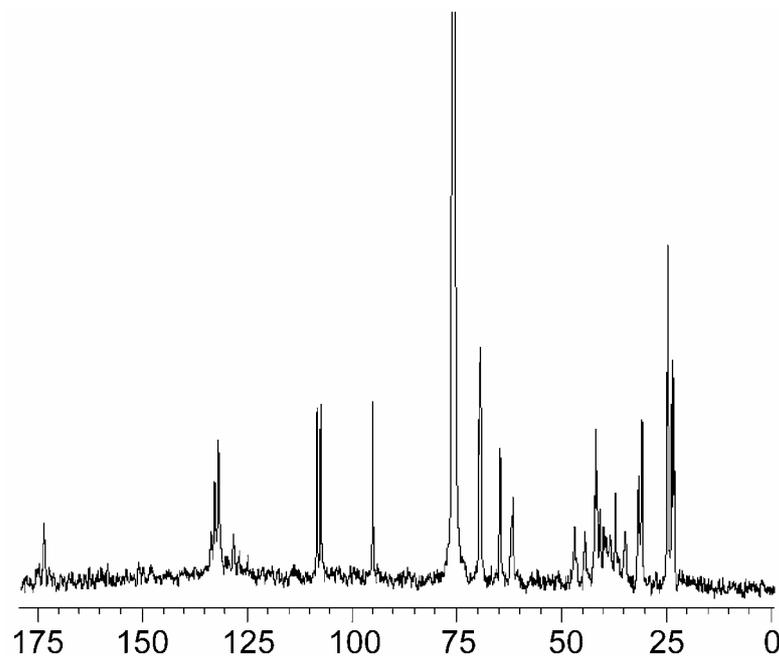


Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

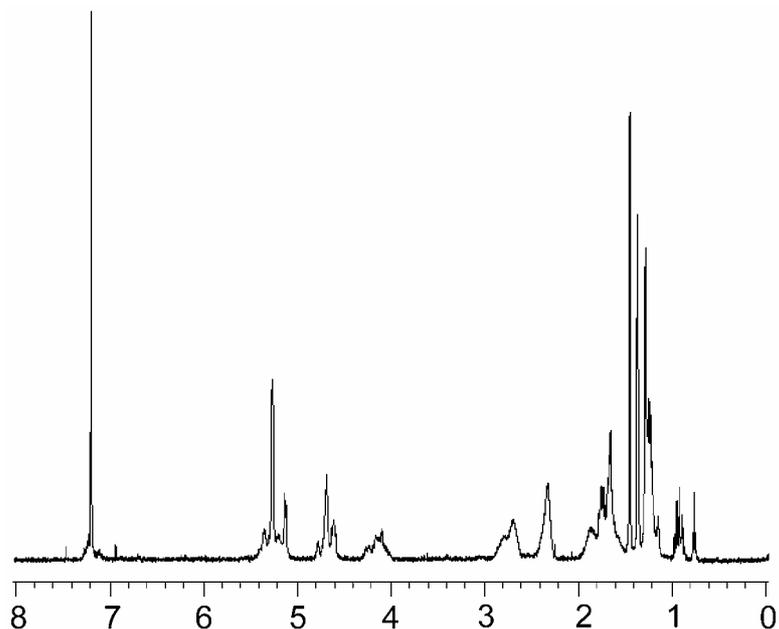
^1H NMR spectrum (in CDCl_3) for poly(macromonomer), poly(4a), corresponding to run 11 in Table 2, ($k = 5$).



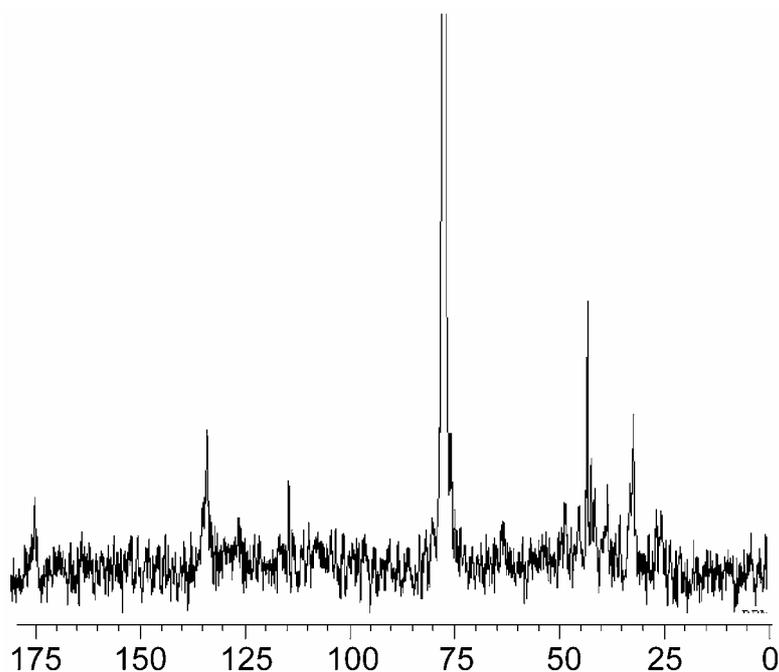
^{13}C NMR spectrum (in CDCl_3) for poly(macromonomer), poly(4a), corresponding to run 11 in Table 2, ($k = 5$).



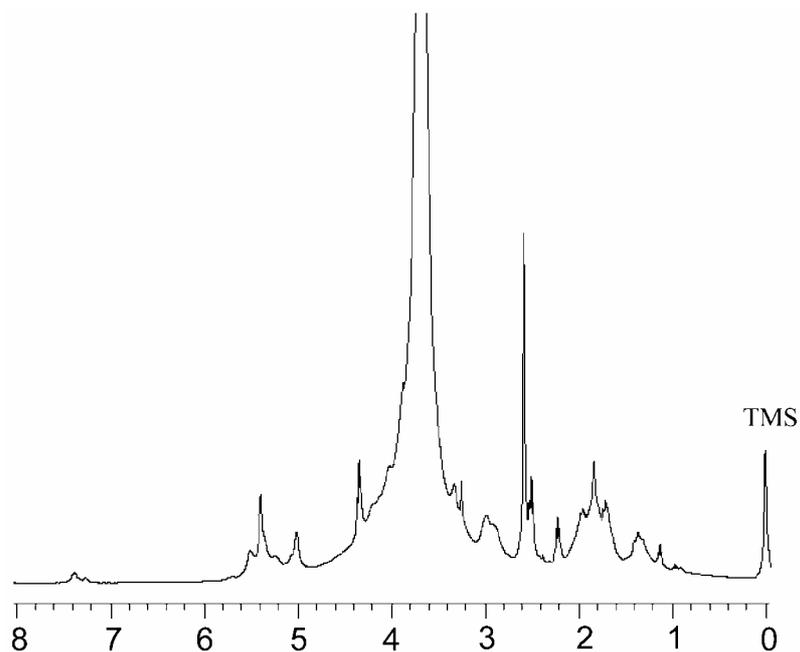
¹H NMR spectrum (in CDCl₃) for poly(macromonomer), poly(4b), corresponding to run 14 in Table 2, (k = 10).



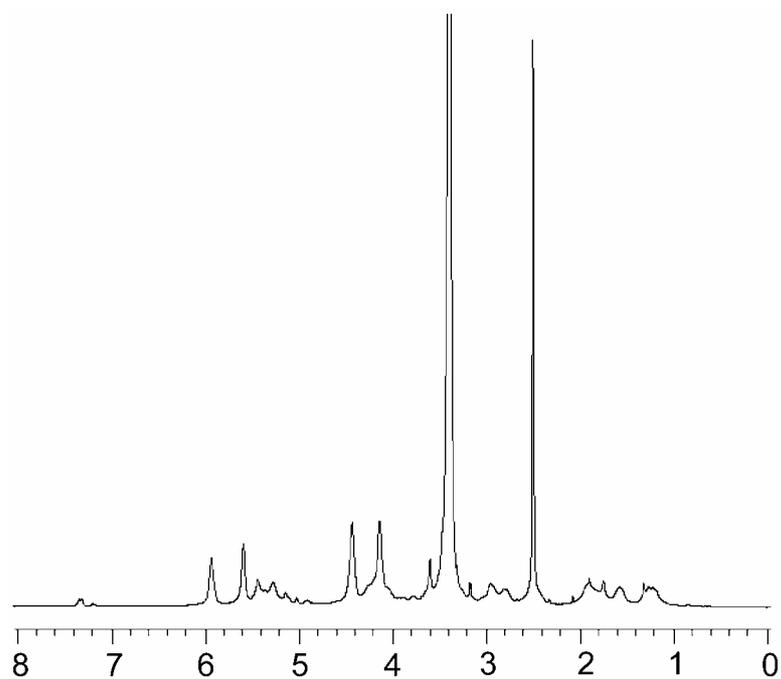
¹³C NMR spectrum (in CDCl₃) for poly(macromonomer), poly(4b), corresponding to run 14 in Table 2, (k = 10).



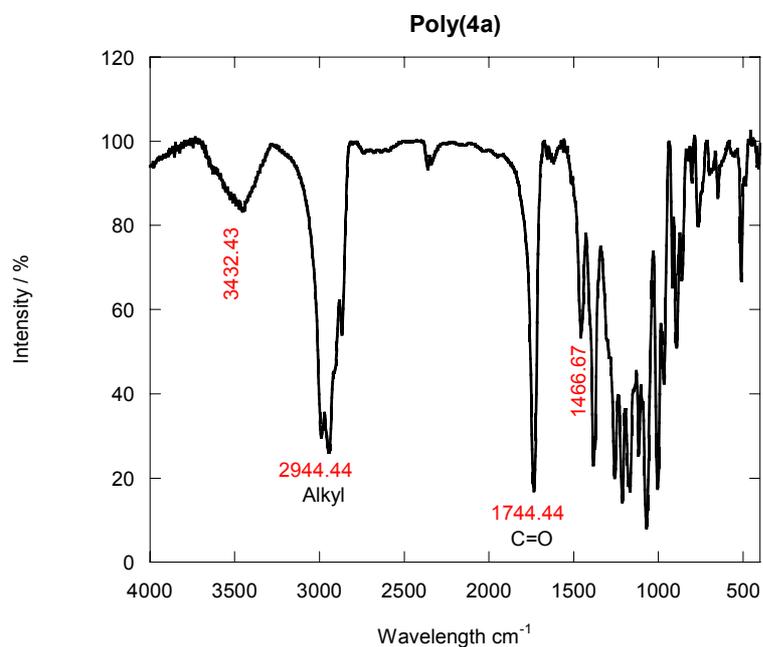
^1H NMR spectrum (in $\text{DMSO-}d_6$) for deprotected poly(macromonomer), poly(5a), corresponding to run 10 in Table 2, ($k = 10$).



^1H NMR spectrum (in $\text{DMSO-}d_6$) for deprotected poly(macromonomer), poly(5b), corresponding to run 14 in Table 2, ($k = 10$).



4. FT-IR spectrum (KBr disk) for poly(**4a**), corresponding to run 10 in Table 2, (k = 10).



FT-IR spectrum (KBr disk) for poly(**5a**), corresponding to run 10 in Table 2, (k = 10).

