Fluorocarbon End-functionalized Polymers from Poly(arylether) Dendritic Initiators

A. Pillay Narrainen, L. R. Hutchings, W. J. Feast, R. L. Thompson,**
I. A. Ansari, N. Clarke

Summary: Fréchet-type poly(arylether) first and second generation (G1 and G2 respectively) dendrons were prepared from 1-(bromomethyl)-3,5-bis(trifluoromethyl)-benzene. The latter and the brominated versions of the two dendrons were successfully employed in the copper mediated living radical polymerization (LRP) of styrene-d_8 giving polymers of predictable molecular weights and narrow polydispersities. Contact angle measurements and ion beam analysis were used to explore the adsorption of these materials to the air-polymer surface in blended films with unfunctionalized hydrogenous polystyrene. Although contact angle analysis indicated only modest changes in the hydrophobicity and lipophobicity of the surface, ion beam analysis clearly showed the formation of an excess layer of dendron functionalized polymer at the exposed surface that increased with increasing fluorine content.

Keywords: contact angles; dendrimers; initiators; ion beam analysis; living radical polymerization; polystyrene

Introduction

The modification of the interfacial or surface properties of polymers can lead to improvements in applications such as coatings, adhesives and biomaterials.[1–3] It is well-known that perfluoroalkyl groups are attracted to an exposed surface of materials due to their low surface energy.[3–5] A practical limitation of the use of fluorocarbon groups to modify hydrocarbon polymers is their poor solubility in most organic solvents.

We report here the synthesis of novel Fréchet-type poly(arylether) dendrons with multiple peripheral CF_3 functionality. The compact globular shape and easily controlled size and functionality of dendrimers make them ideal building blocks for surface related applications.[6,7] Fréchet *et al.* have successfully used poly(arylether) dendrons as LRP initiators for vinylic monomers.[8,9] In this work, brominated dendrons are employed in the copper mediated LRP of styrene-d_8. Thin films, made from blends of these polymers, have been studied by ion beam analysis and contact angle measurements to understand their migration to surfaces.

Experimental

General Procedures

Williamson Ether Coupling Reactions

A mixture of benzyl bromide, 3,5-dihydroxybenzyl alcohol (Aldrich, 99%), potassium carbonate (Aldrich, 99.995%), 18-crown-6 (Aldrich, 99%) and dry acetone were charged in a 2-neck round bottom flask which was previously flushed with nitrogen. The mixture was stirred vigorously and refluxed under nitrogen for 6–24 hours. The reaction mixture was then allowed to cool and was filtered to remove the salt. The solution was evaporated to dryness, dissolved in CH_2Cl_2 and washed

---

Department of Chemistry, University of Durham, Durham DH1 3LE, UK

with water. The water layer was extracted twice with more organic solvent and the combined extracts were dried over magnesium sulfate, filtered and dried under reduced pressure. Further purification by recrystallization was performed.

Bromination Reactions

The benzyl alcohol was dissolved in a minimum of dry THF in a 2-neck round bottom flask fitted with a nitrogen supply. Carbon tetrabromide (Aldrich, 99%) was added followed by the slow addition of triphenylphosphine (Aldrich, 99%). The reaction mixture was stirred at room temperature under nitrogen. The reaction progress was monitored by ^{1}H-NMR and quenched with water upon full conversion. The mixture was evaporated to dryness, dissolved in CH_2Cl_2 and washed with water. The water layer was extracted twice with more organic solvent and the combined extracts were dried over magnesium sulfate, filtered and dried under reduced pressure. Further purification by recrystallization was performed.

Copper Mediated LRP of Styrene-d$_8$

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Cu(I)Br, solid initiator (**3**, **5**) and 2,2′-dipyridyl (1:1:2) were placed together with a magnetic stirrer bar in an oven-dried Schlenk tube. The tube was fitted with a rubber septum and pump filled with nitrogen three times. Styrene-d$_8$ was degassed by bubbling with nitrogen for at least 20 minutes before polymerization. The latter was transferred to the Schlenk tube via syringe. When 1-(bromomethyl)-3,5-bis(trifluoromethyl)benzene (**1**) was used as initiator, it was added at this stage because it is a liquid. The mixture was further degassed by three freeze-pump-thaw cycles. The tube was then lowered into a thermostatically controlled oil-bath at 110 °C and left for 18–24 hours. The polymer mixtures were left to cool and were diluted with toluene. They were then passed over a column of aluminium oxide, precipitated in methanol and dried under vacuum.

Preparation of Dendrons

*(m-F$_3$C)$_4$-[G$_1$]-OH (**2**)*

Prepared from 1-(bromomethyl)-3,5-bis-(trifluoromethyl)benzene (**1**) (Fluorochem, 97 %) (32.3 g, 0.105 mol), 3,5-dihydroxybenzyl alcohol (7.00 g, 0.050 mol), K_2CO_3 (17.6 g, 0.127 mol) and 18-crown-6 (2.65 g, 10.2 mmol). The product was recrystallized from ethanol/water (2:1) to give white crystals.

Yield 26.2 g (88.5 %). M.p. 121–122 °C. (Elemental analysis: Found: C 50.76; H 2.72; F 38.51. Calculated: C 50.69; H 2.72; F 38.49).

δ_H($CDCl_3$) 1.65 (s, 1H, OH), 4.69 (s, 2H, CH_2OH), 5.17 (s, 4H, OCH_2), 6.72 (t, 1H, *J* 2.20 Hz, ArH), 6.69 (d, 2H, *J* 2.00 Hz, ArH), 7.86 (s, 2 × 1H, ArH) and 7.90 (s, 2 × 2H, ArH).

δ_C($CDCl_3$) 65.00 (1C, CH_2OH), 68.57 (2C, OCH_2), 101.40 (1C, ArCH), 106.08 (2C, ArCH), 121.98 (2 × 1C, ArCH), 124.45 (q, 4C, *J* 270 Hz, CF_3), 127.24 (2 × 2C, ArCH), 131.74 (q, 4C, *J* 33 Hz, *C*CF_3), 139.37 (2 × 1C, Ar*C*CH_2O), 144.51 (1C, Ar*C*CH_2OH), 159.53 (2C, ArCO).

*(m-F$_3$C)$_4$-[G$_1$]-Br (**3**)*

Prepared from (*m*-F_3C)$_4$-[G$_1$]-OH (**2**) (2.50 g, 4.22 mmol), CBr_4 (1.75 g, 5.28 mmol) and PPh_3 (1.38 g, 5.28 mmol). Product was recrystallized from ethanol to give white crystals. Yield 2.2 g (79.4 %). M.p. 130–132 °C. (Elemental Analysis: Found: C 45.79; H 2.27; F 34.23; Br 11.08. Calculated: C 45.82; H 2.27; F 34.79; Br 12.19).

δ_H($CDCl_3$) 4.44 (s, 2H, CH_2Br), 5.17 (s, 4H, OCH_2), 6.58 (t, 1H, *J* 2.20 Hz, ArH), 6.70 (d, 2H, *J* 2.40 Hz, ArH), 7.87 (s, 2 × 1H, ArH) and 7.91 (s, 2 × 2H, ArH).

δ_C($CDCl_3$) 32.91 (1C, CH_2Br), 68.63 (2C, OCH_2), 102.29 (1C, ArCH), 108.59 (2C, ArCH), 122.10 (2 × 1C, ArCH), 124.55 (q, 4C, *J* 270 Hz, CF_3), 127.26 (2 × 2C, ArCH), 131.89 (q, 4C, *J* 33 Hz, *C*CF_3), 139.11 (2 × 1C, Ar*C*CH_2O), 140.51 (1C, Ar*C*CH_2Br), 159.43 (2C, ArCO).

(m-F_3C)$_8$-[G_2]-OH (**4**)

Prepared from (*m*-F_3C)$_4$-[G_1]-Br (**3**) (12.0 g, 18.3 mmol), 3,5-dihydroxybenzyl alcohol (1.34 g, 9.58 mmol), K_2CO_3 (9.21 g, 66.6 mmol) and 18-crown-6 (1.96 g, 7.41 mmol). Product was recrystallized from acetone/water (10:1) and washed with cold methanol.

Yield 8.2 g (69.5 %). M.p. 170–171 °C. (Elemental Analysis: Found: C 52.95; H 2.79; F 35.70. Calculated: C 53.12; H 2.82; F 35.38).

δ_H($CDCl_3$) 1.85 (s, 1H, OH), 4.65 (s, 2H, C*H*$_2$OH), 5.03 (s, 4H, OCH_2), 5.16 (s, 8H, OCH_2), 6.54 (t, 1H, *J* 2.20 Hz, ArH), 6.61 (t, 2 × 1H, *J* 2.00 Hz, ArH), 6.64 (d, 2H, *J* 2.00 Hz, ArH), 6.74 (d, 2 × 2H, *J* 2.00 Hz, ArH), 7.86 (s, 4 × 1H, ArH) and 7.91 (s, 4 × 2H, ArH).

δ_C($CDCl_3$) 65.18 (1C, CH_2OH), 68.61 (4C, OCH_2), 69.72 (2C, OCH_2), 101.41 (1C, ArCH), 101.66 (2 × 1C, ArCH), 105.81 (2C, ArCH), 106.70 (2 × 2C, ArCH), 122.01 (4 × 1C, ArCH), 124.56 (q, 4C, *J* 270 Hz, CF_3), 127.22 (4 × 2C, ArCH), 131.85 (q, 4C, *J* 33 Hz, *C*CF_3), 139.27 (4 × 1C, Ar*C*CH_2O), 140.01 (2 × 1C, Ar*C*CH_2O), 143.62 (1C, Ar*C*CH_2OH), 159.57 (2 × 2C, ArCO), 159.99 (2C, ArCO).

(m-F_3C)$_8$-[G_2]-Br (**5**)

Prepared from (*m*-F_3C)$_8$-[G_2]-OH (**4**) (1.50 g, 1.66 mmol), CBr_4 (0.671 g, 2.02 mmol) and PPh_3 (0.529 g, 2.02 mmol). Product was recrystallized from acetone/methanol (1:1) to give white crystals. Yield 1.32 g (84.1 %). M.p. 156–157 °C. (Elemental Analysis: Found: C 50.58; H 2.59; F 33.38; Br 5.39. Calculated: C 50.65; H 2.61; F 33.38; Br 5.91).

δ_H($CDCl_3$) 4.43 (s, 2H, CH_2Br), 5.03 (s, 4H, OCH_2), 5.18 (s, 8H, OCH_2), 6.54 (t, 1H, *J* 2.00 Hz, ArH), 6.62 (t, 2 × 1H, *J* 2.00 Hz, ArH), 6.65 (d, 2H, *J* 2.00 Hz, ArH), 6.74 (d, 2 × 2H, *J* 2.00 Hz, ArH), 7.88 (s, 4 × 1H, ArH) and 7.91 (s, 4 × 2H, ArH).

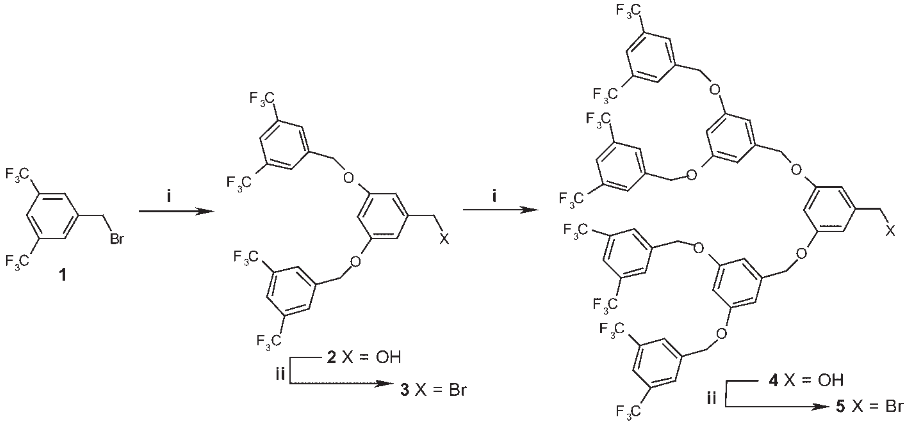
δ_C($CDCl_3$) 33.68 (1C, CH_2Br), 68.82 (4C, OCH_2), 70.02 (2C, OCH_2), 101.92 (2 × 1C, ArCH), 102.50 (1C, ArCH), 106.93 (2 × 2C, ArCH), 108.47 (2C, ArCH), 122.24 (4 × 1C, ArCH), 123.30 (q, 4C, *J* 270 Hz, CF_3), 127.49 (4 × 2C, ArCH), 132.10 (q, 4C, *J* 33 Hz, *C*CF_3), 139.46 (4 × 1C, Ar*C*CH_2O), 139.96 (2 × 1C, Ar*C*CH_2O), 140.26 (1C, Ar*C*CH_2Br), 159.80 (2 × 2C, ArCO), 160.09 (2C, ArCO).

Measurement

NMR spectra were recorded on a Bruker Avance-400 spectrometer. Molecular weights of polymers were determined using a Viscotek TDA 302 with refractive index, viscosity and light scattering detectors and 2 × 300 ml PLgel 5 μm mixed C columns. THF was used as the eluent at a flow rate of 1.0 ml/min and at a constant temperature of 30 °C. The light scattering detector was calibrated with a narrow molecular weight polystyrene standard purchased from Polymer Laboratories. Polymer blends were prepared by co-dissolving dendron functionalized deuterated polystyrene (DPS) and hydrogenous polystyrene ($M_n = 250\,000$ gmol^1, $M_w/M_n = 1.05$) in toluene. The fraction of dendron-functionalized DPS was fixed at 15% (w/w) of the solute. Solvent casting of blended polymer solutions was carried out using a Cammax PRS14E photoresist spinner. Polymer solutions were spin-coated onto silicon substrates and films of approximately 150 nm total thickness were obtained. Annealing of films was carried out at 130 °C for 1 hour under vacuum. Ion beam analysis experiments were carried out on both annealed and unannealed films in order to quantify the extent of surface adsorption of each polymer. Static contact angles were measured at room temperature using a Ramé-Hart goniometer model 100. Angles were measured for annealed and unannealed films using water and dodecane and all data quoted is the average of at least three separate measurements.

Synthesis of Dendrons and Polymers

The strategic plan for the synthesis of the dendrons involved the successive Williamson ether coupling of a trifluoromethyl



1

Scheme 1.
Synthesis of ditrifluoromethyl(benzene)-terminated dendrons. Reagents: (i) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, acetone, reflux; (ii) CBr_4, PPh_3, THF.

decorated benzyl bromide with 3,5-dihdroxylbenzyl alcohol and bromination of the core benzylic alcohol functionality to generate an 'active' dendron which can be used for generation growth (Scheme 1), analogous to the methodolgy developed by Fréchet *et al.*[10,11] The dendrons prepared were obtained in good yields by recrystallization.

The use of benzyl bromide dendrons for the copper mediated LRP of styrene has been previously demonstrated Fréchet *et al.*[8,9] We employed a Cu(I)Br/bipyridine catalyst for the polymerization of styrene-d_8 from bromo-initiators **1**, **3** and **5**. Polymer molecular weights were close to the target molecular weights and with polydispersities between 1.1–1.4. A summary of the polymers made is given in Table 1. Initiator peaks can be seen in the ^{1}H NMR of the purified polymers indicating the attachment of the polymer to the initiator. The incorporation of the initiator into the polymer is further confirmed in the ^{19}F NMR spectra of the polymers where a single peak at −64.2 ppm is observed. Two polymers with target molecular weights 10 000 g/mol (10k) and 15 000 g/mol (15k) were prepared from initiator **5** to investigate the effect of molecular weight on surface adsorption.

Table 1.
Deuterated polystyrene samples prepared.

Initiator used	Deuterated polystyrene (DPS) Sample	Target M_n	M_n	M_w/M_n
1	**1**DPS (10k)	10 000	8 800	1.33
3	**3**DPS (10k)	11 700	10 500	1.26
5	**5**DPS (10k)	10 000	9 200	1.26
5	**5**DPS (15k)	15 000	15 600	1.14

Ion Beam Analysis

Nuclear reaction analysis was used to investigate the surface adsorption behavior of these additives. This is a technique which allows the absolute determination of concentration of the deuterium labeled additive with respect to depth of the film. By judicious choice of sample orientation and beam energy, depth resolution better than 10 nm is routinely possible and therefore appropriate for the characterisation of surface excess layers. Experiments were carried out using an NEC 5SDH pelletron ion beam accelerator. A beam of $^3He^+$ ions was accelerated to 0.7 MeV and directed onto the sample surface at 83° to the sample normal ("grazing incidence"). Backscattered protons arising from the d(3He,p)α nuclear reaction[12] were detected at 170° to the incident beam. The beam diameter was 2 mm, and measurements were taken over a total charge of 5 μC $^3He^+$. Proton spectrum data were converted to volume fraction of deuterated polymer versus depth according to the thick target approximation.[13] Data were fitted with a simple 2-slab model concentration profile, comprising a thin upper layer describing the deuterated polymer concentration at the surface of the film, and a thicker lower layer describing the bulk of the film. The surface concentration of the upper layer and the thickness of the lower layer were non-linearly least-squares fitted to each data set to obtain the nominal surface concentration and total film thickness. Typical experimental data and model fit are shown in Figure 1. The instrumental resolution of the measurement was approximately 6 nm at the film surface and becomes poorer with increasing depth.

The surface excess, z^*_{i}, of the adsorbed polymer i is the parameter of fundamental thermodynamic interest, and is defined as

$$z*_i = \int_0^\infty \phi_i(x) - \phi_{i,bulk} dx$$

where ϕ_i is the volume fraction of component i as a function of depth, x, and $\phi_{i,bulk}$ is the bulk concentration of i. The surface excess is a measure of the amount by which the concentration of functionalized polymer at the surface exceeds the bulk concentration. For the two-slab model used to fit the data, this simplifies to

$$z*_i = h(\phi_{i,surface} - \phi_{i,bulk})$$

where h is the thickness of the upper layer in the model. The measured value of z^* has previously been shown to be independent of the choice of h, provided that h does not greatly exceed the instrumental resolution.[14] Surface excess data obtained in this analysis are summarized in Table 2. It is sometimes convenient to consider the surface excess in terms of the effective area at the surface per adsorbed chain, A, where $A = V/z^*$ (V = volume of each DPS chain).

The tabulated data clearly demonstrate that the surface activity of the dendron functionalized DPS increases with both annealing of the film and the number of CF_3 groups per polymer chain. Interestingly, no evidence whatsoever was found for an excess of DPS chains grown from bromo-initiator **1**, having just two CF_3 groups. The formation of a surface excess in the unannealed blended films indicates some surface activity of the functionalised DPS in the solution as well as in the dry blended film. The surface excess values appear to increase by a factor of approximately 2 with increasing CF_3 group number

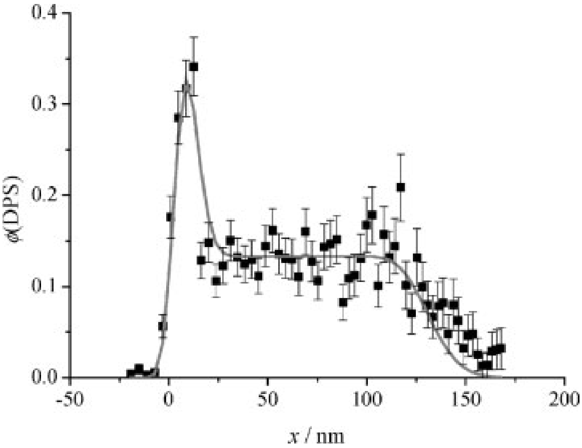


Figure 1.

DPS concentration profile for **5**DPS (15k) blend obtained via nuclear reaction analysis. The peak close to the surface (x = 0) indicates the excess of this material found at the surface after annealing. The solid curve indicates the best fit obtained using a two-slab model concentration profile.

Table 2.
Surface excess data obtained from nuclear reaction analysis of blended films. The thickness of the excess layer of the model and the bulk volume fraction of DPS were fixed at 4 nm and 0.15 respectively. The volume of each DPS chain (V) was estimated from the weight-average molecular weight assuming a density of 1.12 g/cm^3.

Sample	V/nm^3	ϕ_{surface}	z^*/nm	A/(nm^2/chain)
1DPS (10k) unannealed	17.35	0.15	0.00	—
1DPS (10k) annealed	17.35	0.15	0.00	—
3DPS (10k) unannealed	19.61	0.28	0.52	37.98
3DPS (10k) annealed	19.61	0.55	1.61	12.16
5DPS (10k) unannealed	17.19	0.40	0.99	17.30
5DPS (10k) annealed	17.19	0.87	2.89	5.94
5DPS (15k) unannealed	26.37	0.56	1.64	16.11
5DPS (15k) annealed	26.37	1.02	3.49	7.55

from four to eight per polymer. We can see an interesting dependence of surface excess on molecular weight of DPS chain for the two polymers synthesized from bromo-initiator **5**. The surface excess (z^*) of the larger polymer chain is consistently slightly larger than for the smaller chain whether the sample is annealed or not. However, when the surface excess value is normalized to take into account the volume of the DPS chain, the effective area per adsorbed polymer chain (A) is smaller for the smaller chain. This suggests that the maximum number of CF_3 groups adsorbed per unit area, which is proportional to $1/A$, increases with decreasing DPS polymer molecular weight.

Contact Angles

Contact angles with water and dodecane were measured for films made from the pure functionalized polymers and 15% (w/w) blends. The polystyrene matrix used in the blends gave a contact angle of 90° with water whereas dodecane spread on the surface of the film making the angle unmeasurable.

Table 3 shows that **1**DPS (10k) does not affect contact angles as compared to unfunctionalized polystyrene. This is consistent with the absence of any measurable surface excess from the nuclear reaction analysis. The relatively modest change in contact angle for the **3**DPS and **5**DPS films is slightly more surprising, given the surface-activity that is apparent from nuclear reaction analysis. However, we should note that even in the case of the most surface-active material, the effective area per adsorbed molecule was approximately 6 nm^2 per chain. The effective area per CF_3 group can be estimated from the cross-sectional area perfluorocarbon chain to be approximately 0.28 nm^2. In this case

Table 3.
Contact angles for annealed and unannealed films. Angles were reproducible to within ±2°.

Sample	Unannealed films		Annealed films	
	water	dodecane	water	dodecane
Blend **1**DPS (10k)	90°	Drop spreads	90°	Drop spreads
100% **1**DPS (10k)	90°	Drop spreads	90°	Drop spreads
Blend **3**DPS (10k)	90°	Drop spreads	92°	4°
100% **3**DPS (10k)	90°	Drop spreads	91°	4°
Blend **5**DPS (10k)	96°-drops to 92° after a minute	9°	95°-drops to 92° after a minute	10°
100% **5**DPS (10k)	93°	5°	100°-drops to 92° after 2 minutes	15°
Blend **5**DPS (15k)	90°	4°	90°	4°
100% **5**DPS (15k)	90°	4°	90°	4°

the surface coverage is at most 37 % CF_3, possibly less if some proportion of the CF_3 groups cannot reach the polymer surface. Finally, we should note that the CF_3 group has a small dipole due to the tetrahedral arrangement of the electronegative F atoms. Although adsorption of the CF_3-functionalised polymer must reduce the overall surface energy, it is possible that this process leads to a slight increase in the polarity of the surface. This may explain the relatively small change in contact angle with respect to water (a polar solvent) when compared to our results for dodecane.

The increasing dodecane contact angle with increasing surface adsorption of the additive in the blend is consistent with a reduction in surface energy. The largest angle ($\sim 10^\circ$) was measured for **5**DPS (10k) which agrees with nuclear reaction analysis data as the highest number of CF_3 groups adsorbed per unit area was obtained for this polymer. The reason for the unstable contact angle measurements with respect to water for the strongly adsorbing systems is not yet clear. This is an intiguing situation, and suggests that even though the polymer films are glassy, some local reorganisation at the film surface may be possible, allowing a reduction in the number of unfavouable contacts between CF_3 groups and water.

Conclusion

We have herein synthesized a series of well-defined CF_3 end-functionalized deuterated polystyrene. Nuclear reaction analysis on thin films of blends of these polymers has shown that there is a surface excess of functional polymers with four and eight CF_3 groups. Surface excess was found to increase with annealing and the number of CF_3 groups. The number of chains adsorbed per unit area was also found to increase with decreasing polymer molecular weight for annealed films. Contact angle analysis with polar and non-polar solvents is broadly consistent with the observed surface excess behavior, and indicates that the CF_3 groups may impart an additional degree of polarity to the modified polymer surface.

Acknowledgement: The authors are grateful to the European Union, Nanotech UIC and One Northeast for financial support. We also wish to thank Dr. A. M. Kenwright for NMR analysis.

[1] C. Y. Kim, J. Evans, D. A. I. Goring, *J. Appl. Polym. Sci.* **1971**, *15*, 1365.
[2] H. Z. Zhuang, J. A. , Jr. Gardella, *Macromolecules* **1997**, *30*, 3632.
[3] W. K. Lee, I. Losito, J. A. , Jr. Gardella, W. L. , Jr. Hicks, *Macromolecules* **2001**, *34*, 3000.
[4] K. Sugiyama, T. Nemoto, G. Koide, A. Hirao, *Macromol Symp.* **2002**, *181*, 135.
[5] A. Hirao, S. Sakai, K. Sugiyama, *Polym. Adv. Technol.* **2004**, *15*, 15.
[6] J. M. J. Fréchet, *Science* **1994**, *263*, 1710.
[7] D. C. Tully, J. M. J. Fréchet, *Chem. Commun.* **2001**, 1229.
[8] M. R. Leduc, C. J. Hawker, J. Dao, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1996**, *118*, 11111.
[9] M. R. Leduc, W. Hayes, J. M. J. Fréchet, *J. Polm. Sci., Part A* **1998**, *36*, 1.
[10] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638.
[11] C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc. Chem. Comm.* **1990**, *15*, 1010.
[12] R. S. Payne, A. S. Clough, P. Murphy, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms* **1989**, *42*, 130.
[13] R. J. Composto, R. M. Walters, J. Genzer, *Materials Science and Engineering R* **2002**, *R38*, 107.
[14] F. T. Kiff, R. W. Richards, R. L. Thompson, *Langmuir* **2004**, *20*, 4465.