Multi-armed, TEMPO-functionalized unimolecular initiators for starburst dendrimer synthesis via stable free radical polymerisation. 2. Tris (1,3,5)benzyloxy unimers[1]

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Abstract: The synthesis of the trifunctionalized TEMPO-modified unimolecular initiators, unimers I, II, and III is described. Unimer I was prepared via an S_N2 type Williamson ether coupling of 1,3,5-tris(iodomethyl)benzene with a TEMPO-containing ethylbenzene hydroxy derivative. The synthesis of unimer II, however, was accomplished through S_N1 reaction of 1,3,5-tris(bromomethyl)benzene with the hydroxy-ethylbenzene TEMPO derivative in the presence of silver triflate. Synthesis of unimer III started from phloroglucinol and an S_NAr reaction with 1-fluoro-4-nitrobenzene, followed by reduction to the amino compound and Schiff base formation with the TEMPO-derivatized aromatic aldehyde. Stable free radical polymerisation (SFRP) of styrene and acetoxystyrene with unimer I are also described with molecular weights and polydispersities reported. It is concluded that the SFRP of styrene with a triradical initiator meets the requirements of a living system.

Key words: stable free radical polymerisation, starburst dendrimer, multi-armed unimolecular initiators.

Résumé : On décrit la synthèse d'initiateurs unimoléculaires trifonctionnalisés à base de 2,2,6,6-tétraméthylpipéridinyloxyle (TEMPO), les unimères I, II et III. L'unimère I a été préparé par le biais d'une réaction S_N2, de type formation d'éther de Williamson, par le couplage du 1,3,5-tris(iodométhyl)benzène avec un dérivé hydroxylé de l'éthylbenzène portant le radical TEMPO. Toutefois, la synthèse de l'unimère II a été réalisée par le biais d'une réaction S_N1 du 1,3,5-tris(iodométhyl)benzène avec le dérivé hydroxylé de l'éthylbenzène portant le radical TEMPO, en présence de triflate d'argent. La synthèse de l'unimère III a été réalisée à partir du phloroglucinol et une réaction S_NAr avec le 1-fluoro-4-nitrobenzène, suivie d'une réduction en dérivé amino et de la formation d'une base de Schiff avec un aldéhyde aromatique portant le radical TEMPO. On décrit aussi la polymérisation avec un radical libre stable du styrène et de l'acétoxystyrène catalysée par l'unimère I et on rapporte les poids moléculaires et les polydispersités moyennes. On conclut que la polymérisation avec un radical libre stable du styrène catalysée par un initiateur triradicalaire satisfait les besoins d'un système vivant.

Mots clés : polymérisation avec un radical libre stable, dendrimère en « éclatement d'étoile », initiateur unimoléculaire tentaculaire.

[Traduit par la Rédaction]

Introduction

The achieving of controlled architecture in macromolecules is at the forefront in the synthesis of novel materials with improved properties. In the realm of polymers, profound changes in properties accompany the introduction of branches into the polymer backbone, which leads to the formation of graft or star polymer systems.

The present work forms part of a series of investigations where controlled architecture in a star polymer is achieved through stable free radical polymerisation (SFRP) using the stable nitroxide radical 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (1). Our approach is to synthesize unimolecular initiators containing the TEMPO unit, termed unimers, which are then employed in synthesis of star polymers and copolymers. We describe here the synthesis of three trifunctionalized unimers (I, II, III). The polymerisations of styrene and acetoxystyrene with unimer I to form homopolymers and co-

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polymers are also described. This work is a continuation of our structure-property studies of functionalized dendrimers (2).

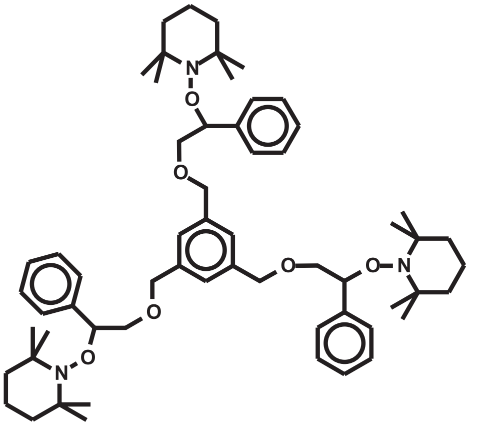
Results and discussion

Unimolecular initiator I synthesis

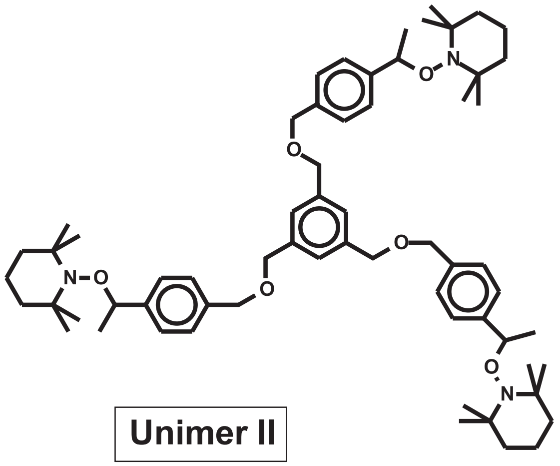
The synthesis of unimer I consisted of a three-step sequence (Scheme 1): (*i*) The benzyloxyamine ester **1** was first prepared by a modification of the method reported by Veregin (3), Hawker (4), Kobatake (5), and their co-workers, by heating benzoyl peroxide and TEMPO with excess styrene at 80 °C for 30 min (82% yield after recrystallization from 2-propanol). (*ii*) Saponification of **1** (4, 6) by heating at reflux with 2 mol L^{-1} KOH in ethanol and flash chromatography gave the alcohol **2** as a light yellow oil (97%). (*iii*) Williamson ether coupling of **2** with 1,3,5-tris(iodomethyl)benzene in THF under reflux (24 h) in the presence of sodium hydride, after flash chromatographic separation, gave unimer I as a light yellow thick syrup (97%).

Unimolecular initiator II synthesis

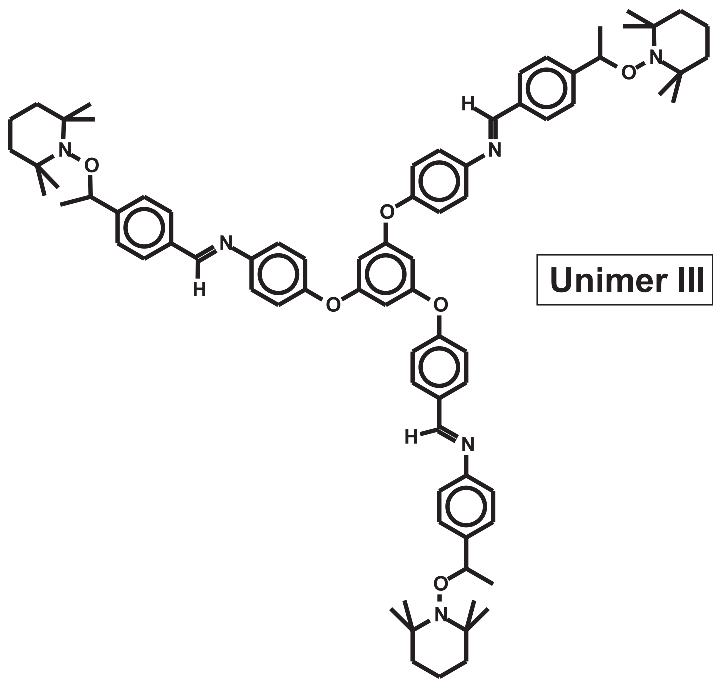
The unimer II was prepared by the following sequence (Scheme 2): (*a*) Initially the benzyloxamine derivatives **3** (X = H, CH_2Cl, CH_2Br, CH_2I, CH_2OH) were synthesized starting with commercially available ethylbenzene derivatives and using modifications of the methods of Georges and co-workers (7), Hawker et al. (8), Priddy and co-workers (9), and Miura et al. (10). In our hands the highest yield of **3** (X = H), 93% after crystallization from ethanol, was obtained by reacting ethylbenzene with *tert*-butyl peroxyoxalate and TEMPO (10); (*b*) in an alternative method, use of Jacobson's catalyst (Salem (10, 11)) with the ethylbenzene derivatives in the presence of di-*tert*-butyl peroxide, sodium



Unimer I

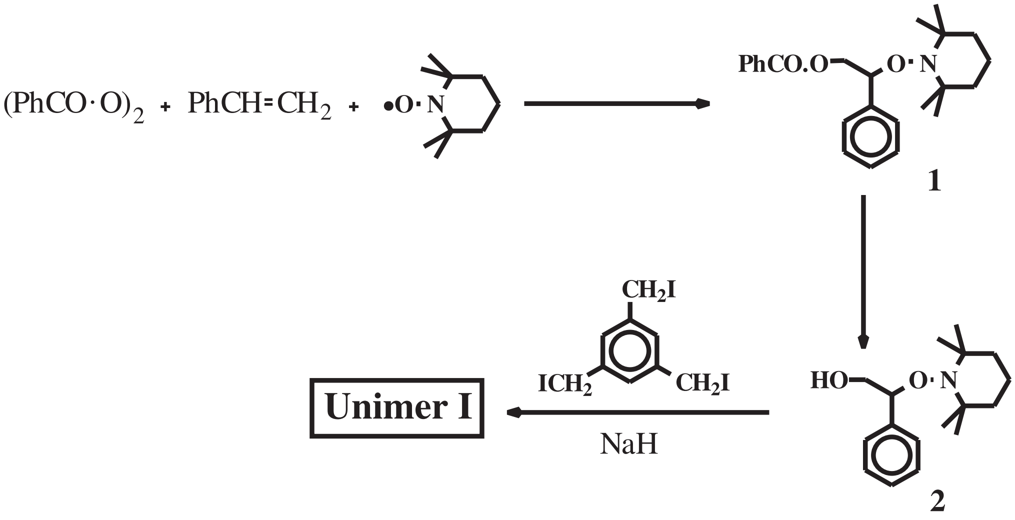


Unimer II

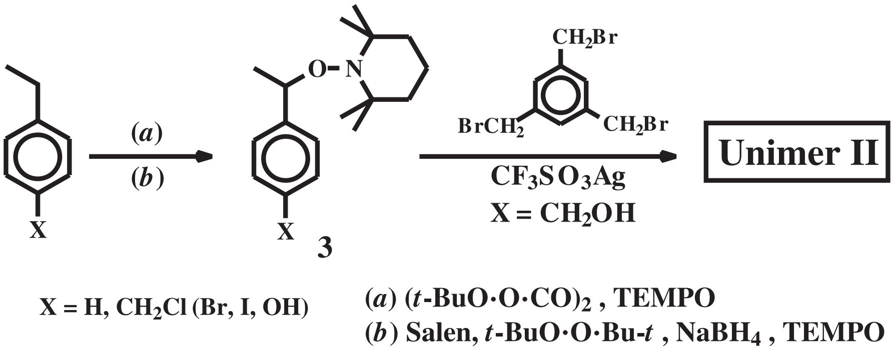


Unimer III

Scheme 1.



Scheme 2.



borohydride, and TEMPO (12) gave alkoxyamines **3** in yields ranging over 20% (X = CH_2Cl), 41% (X = H), and 51% (X = CH_2OH). Attempted formation of unimer II through S_N2 Williamson ether coupling of **3** (X = CH_2OH) with 1,3,5-tris(iodomethyl)benzene as in the case of unimer I, was unsuccessful in our hands. The preparation of unimer II was then accomplished via an S_N1 type reaction of 1,3,5-tris(bromomethyl)benzene with **3** (X = CH_2OH) in the presence of silver triflate (17% after column chromatographic separation).

Unimolecular initiator III synthesis

The reaction scheme followed the sequence shown in Scheme 3.

(1) The triamine core **4** was obtained in two steps: an S_NAr reaction between 1,3,5-trihydroxy-benzene and 1-fluoro-4-nitrobenzene in the presence of KF in DMSO produced the 1,3,5-tris(4-nitrophenyl)benzene derivative **4**-NO_2 in 50% yield. The triamino core **4**-NH_2 was then obtained through Fe–HCl reduction in 94% yield after purification.

(2) Unimer III was obtained as the Schiff base adduct on reaction of the triamino core compound **4**-NH_2 with the benzyloxyamine derivative **3** (X = CHO) (85% yield after column chromatographic purification).

Controlled free radical polymerisation of unimolecular initiator I

Polystyrene starburst dendrimer I

Two polymerisations of styrene were performed with Unimer I under bulk conditions at 135 °C, **SFRP 1** and **SFRP 2**. The progress of the SFRP processes was monitored by withdrawal of aliquots from the reaction mixture at different times for % conversion and molecular weight determinations.

In the first polymerisation (**SFRP 1**), 1200 equiv. of styrene to 1 equiv. of unimer I were used under the above conditions for 3 h. The polymer was precipitated from methanol to give star polystyrene with terminal TEMPO end groups (**PS-3T1**), as a white solid (15 g), average molecular weight (M_n) 34 200 and polydespersity (PD) 1.29.

The second polymerisation (**SFRP 2**) was performed using 400 equiv. of styrene to 1 equiv. of unimer I for 4 h to give **PS-3T2** (8.70 g) after precipitation from methanol. The polystyrene had a M_n value of 12 700 and a PD of 1.34.

The ^1H NMR for both polymer samples showed broad peaks between 1.50 and 1.87 ppm representing the methylene and methine protons. Aromatic protons of polystyrene appear as a broad multiplet between 6.49 and 7.10 ppm.

The polymerisation results are shown in Table 1. The conversion-time relationship is plotted for the formation of

Scheme 3.

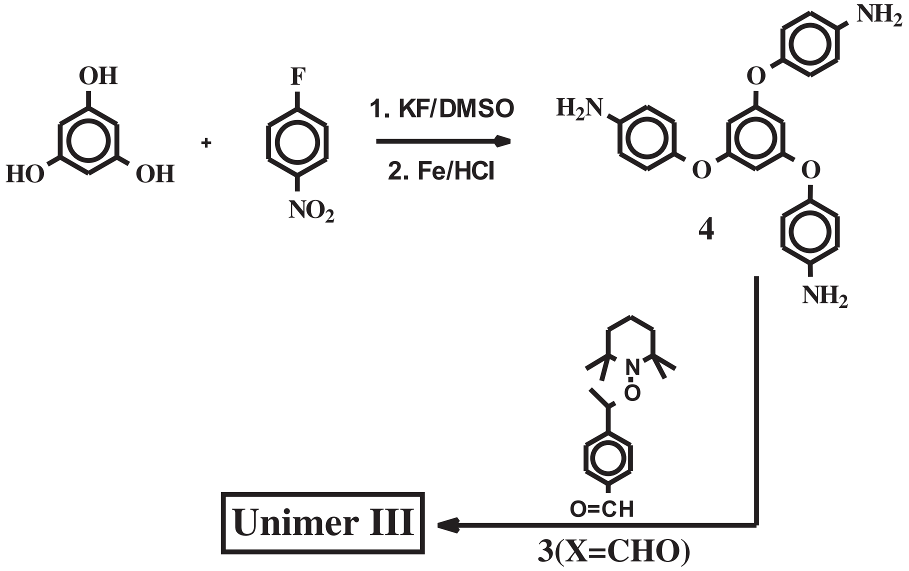


Table 1. Polymerisation results with unimer I.

Method	Time	Conversion[a] (%)	M_n[b] (Theo.)	M_n[c] (Exptl., GPC)	PD[d] (GPC)
SFRP 1					
	30	10	12 320	12 390	1.20
	60	18	21 290	21 040	1.17
	120	45	54 180	28 080	1.28
	180	51	60 760	34 150	1.29
SFRP 2					
	30	12	4 800	5 685	1.25
	60	24	9 600	8 951	1.23
	120	38	15 200	11 690	1.27
	180	48	19 200	14 350	1.27
	240	53	21 200	12 710	1.34

[a] Based on TGA.

[b] Calculation of M_n (Theo.): (*i*) for **SFRP 1**: M_n (Theo.) = conversion (%) × molecular weight (monomer) × 1200 (ratio of styrene to unimer I); (*ii*) for **SFRP 2**: M_n (Theo.) = conversion (%) × molecular weight (monomer) × 400 (ratio of styrene to unimer I).

[c] Estimated by GPC based on polystyrene standards.

[d] PD = M_n/M_w estimated by polystyrene standards.

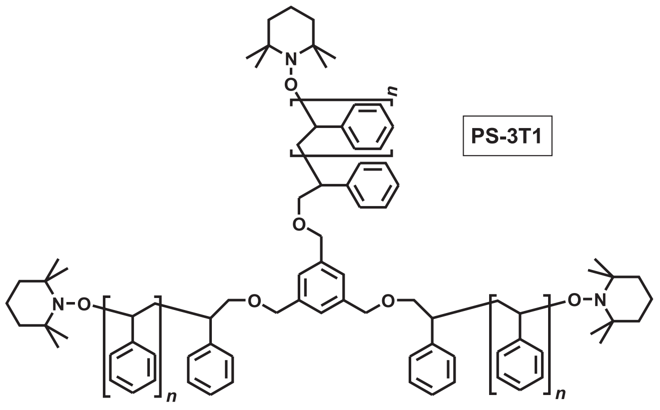
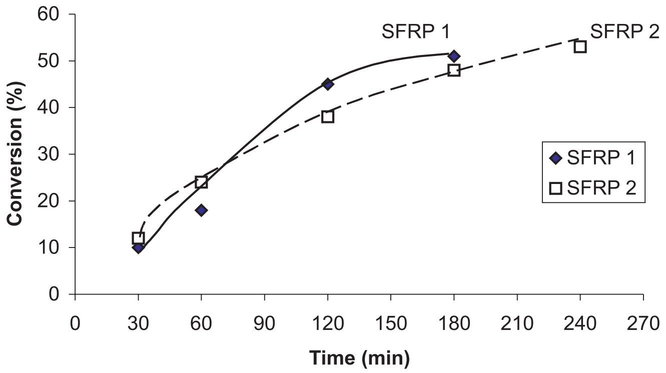
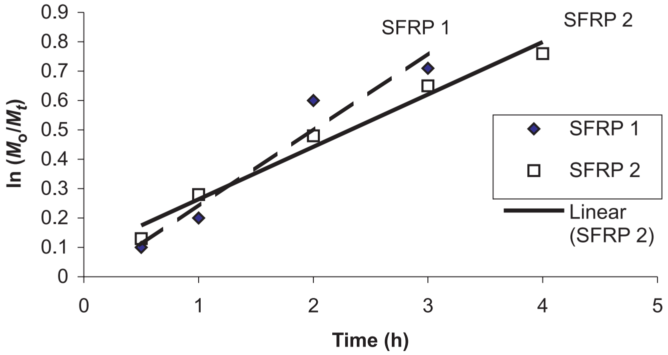


Fig. 1. Plot of % conversion vs. time for **SFRP 1** and **SFRP 2** with unimer I.



PS-3T1 and **PS-3T2** in Fig. 1. As the polymerisation time increases, monomer conversion also increases. Even though the ratio of styrene : unimer I for **SFRP 1** and **SFRP 2** is 3:1, the rate of conversion is almost constant for the two polymerisations. Thus, the polymerisation rate is independent of unimer I concentration.

Fig. 2. Semilogarithmic plot of conversion with reaction time for the SFRP processes with varying initial concentration for **SFRP 1** and **SFRP 2**.



A kinetic plot in semilogarithmic coordinates showing the variation of monomer consumption with time is presented in Fig. 2. M_o represents the initial monomer concentration while M_t is the concentration after time t. Thus, the SFRP of styrene at 135 °C with a triradical initiator (unimer I) meets the requirement of a living system.

Number average molecular weights (M_n) and polydispersities were determined by GPC with polystyrene standards. The plot of the theoretical and experimental M_n data against % conversion are shown in Figs. 3 and 4 for **SFRP 1** and **SFRP 2**, respectively. The experimental M_n data are very close to the calculated theoretical values at the early stages of the polymerisation, which indicates that the formed styryl radicals initiated all growing chains at the same time. There are large deviations of M_n compared with the theoretical values after 40% conversion, which suggests that determination of molecular weight using polystyrene standards (linear chains) is not suitable for star polystyrene. At higher molecular weights the multi-armed polystyrene has a totally different structure and properties compared to the linear analog and will have less hydrodynamic volume. In a related SFRP study with a trifunctionalized unimer, Hawker (13) found that the experimental M_n = 16 500 of the star polymer was lower than the theoretical value (M_n = 21 000). However, when the star polymer was hydrolyzed and the molecular weight of the individual arms measured it was fully consistent with the proposed structure and that each arm of the initiator can actively initiate the monomer similar to the monoinitiator system.

Polyacetoxystyrene starburst dendrimer I

The polymerisation of acetoxystyrene (400 equiv. to 1 equiv. of unimer I) was effected under bulk conditions at 135 °C for 3 h. The polymer was precipitated from methanol to give 5.0 g of a white solid (**PAS-3T**) with an average molecular weight of 21 100 and a PD of 1.30. The ^{1}H NMR shows broad peaks between 1.78 and 1.40 ppm representing the aliphatic protons and a broad multiplet between 7.08 and 6.33 ppm for the aromatic protons of polyacetoxystyrene. The methyl protons of the acetoxy group appear as a singlet at 2.81 ppm. The ^{13}C NMR shows a peak at 169.2 ppm for the carbonyl carbon and 21.23 ppm for the methyl carbon of the acetate group.

Fig. 3. Theoretical and experimental molecular weights for **SFRP 1** plotted against % conversion.

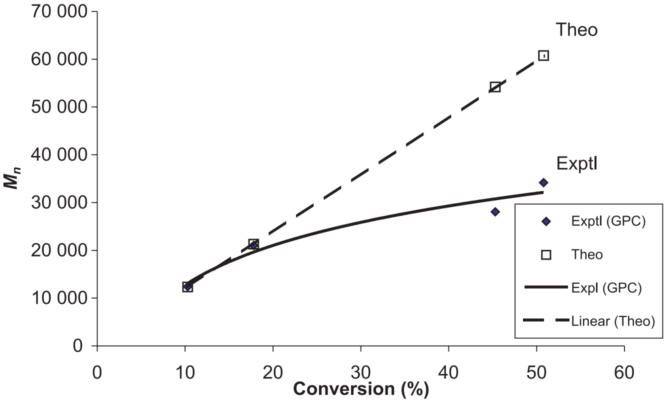
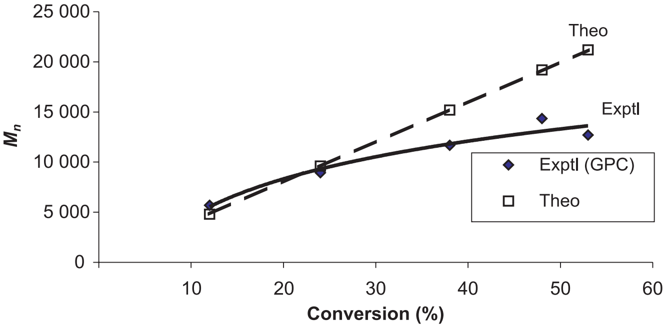


Fig. 4. Theoretical and experimental molecular weights for **SFRP 2** plotted against % conversion.



Hydrolysis of polyacetoxystyrene starburst dendrimer I

Removal of the acetyl group from **PAS-3T** was carried out in methanol by treatment with ammonium hydroxide (15) to give a light yellow solid with an average molecular weight of 16 500 and a PD of 1.23. The decrease in average molecular weight in comparison to **PAS-3T** (M_n = 21 100) is in good agreement with calculated values for deacetylation. The ^{1}H NMR shows the disappearance of the singlet at 2.81 ppm for the methyl protons of the acetoxy group; also, the disappearance of the carbonyl carbon and the methyl group carbon peaks at 196.2 and 21.23 ppm, respectively, confirming that the hydrolysis is complete.

Starburst block copolymer (styrene–acetoxystyrene) dendrimer I

The synthesis of block copolymer was undertaken from **PS-3T1**. A diblock copolymer was obtained via the SFRP technique using 4-acetoxystyrene (25 mL) as the feed monomer at 135 °C for 4 h. A white powder precipitated from methanol (26 g, M_n 95 500, and PD 1.23). The ^{1}H NMR shows two broad peaks at 7.10 and 6.25 ppm corresponding to the protons of the aromatic rings of polystyrene and polyacetoxystyrene, while an intense peak at 2.25 ppm represents the methyl protons of the acetyl group.

Conclusions

The synthesis of unimers I, II, and III was accomplished by reaction sequences outlined in Schemes 1, 2, and 3. Each unimer contains one stereogenic center at the TEMPO junction and the products are obtained as complex diastereomeric mixtures.

The polymerisation of styrene and acetoxystyrene was effected with unimer I to form homopolymers and copolymers. For styrene, two polymerisations (**SFRP 1** and **SFRP 2**) were done using different ratios of unimer I to styrene. A polymer with a M_n of 34 200 and a PD of 1.29 was produced from **SFRP 1** while **SFRP 2** yielded a polymer with a M_n of 12 700 and a PD of 1.34. Conversion-time relationships for **SFRP 1** and **SFRP 2** were plotted and an equivalent rate of polymerisation in both cases was obtained, i.e., the rate is independent of unimer I concentration. Linear semilogarithmic kinetic plots of monomer consumption vs. time were obtained, which meets the requirements of a living system. On plotting the theoretical and experimental M_n data against % conversion, the experimental data correlate with theoretical at low M_n while a variance at higher M_n values is in accord with the star-shaped structure of the polymer.

With acetoxystyrene, unimer I gave a polymer (**PAS-3T**) with a M_n of 21 100 and a PD of 1.30. This was hydrolyzed to yield the hydroxystyrene polymer (**PHS-3T**) with a M_n of 16 500 and a PD of 1.23.

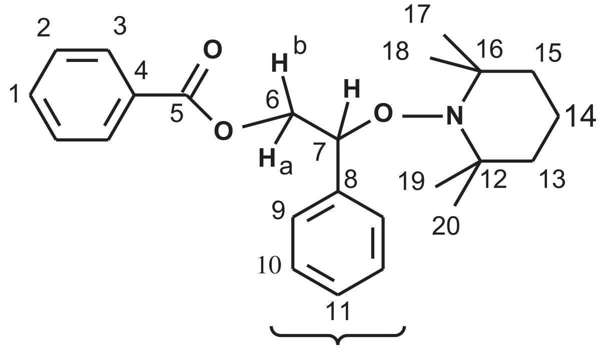
A star block copolymer of styrene and acetoxystyrene was obtained from polymerisation of **PS-3T** with acetoxystyrene to give a polymer with a M_n of 95 500 and of PD 1.23.

Experimental section

Unimer I

Phenethyloxy(2,2,6,6-tetramethylpiperidino)benzoate 1

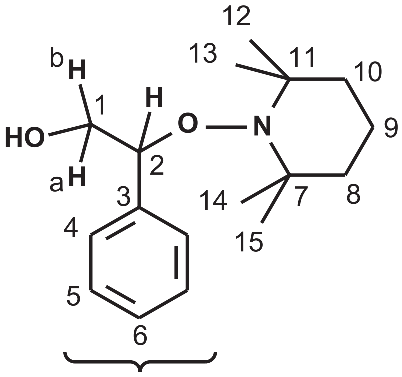
A solution of TEMPO (3.43 g, 22.0 mmol) and BPO (8.0 g, 33.0 mmol) in repurified styrene (150 mL) in a round-bottomed (RB) flask was heated under argon at 80 °C for 30 min while stirring, during which period the solution changed from red to light yellow. After cooling, excess styrene was removed under reduced pressure at ca. 50 °C and the residue was purified by flash column chromatography using CH_2Cl_2 as the eluant to give a pale yellow oil. Recrystallization from 2-propanol yielded **1** as a white solid (7.0 g, 82%), mp 72 °C (lit. value (5) mp 72.2–72.6 °C). IR (KBr disk, cm^{-1}): 2928, 1713, 1460, 1371, 1264, 1129, 1100, 997, 700. ^1H NMR ($CDCl_3$) δ: 7.95 (2H, d, $J_{H\text{-}H}$ ortho = 6.9, H_3), 7.57–7.26 (8H, m, H_{aryl}, $H_{1,2}$), 5.09 (1H, app. t (overlapping d, d), J_{6b7} = 6.3, J_{6a7} = 5.1, H_7), 4.85 (1H, d, d, J_{6a6b} = 11.1, J_{6a7} = 5.1, H_{6a}), 4.55 (1H, d, d, J_{6a6b} = 11.1, J_{6b7} = 6.3, H_{6b}), 1.66–1.02 (6H, m, $H_{13,14,15}$), 1.39, 1.23, 1.09, 0.78 (12H, br s, $H_{17,18,19,20}$). ^{13}C NMR ($CDCl_3$) δ: 166.38 (C_5), 140.76 (C_8), 132.88 (C_9), 130.24 (C_4), 129.63 (C_3), 128.33, 128.10 ($C_{1,11}$), 127.68 ($C_{2,10}$), 84.01 (C_7), 66.83 (C_6), 60.16 ($C_{12,16}$), 40.48 ($C_{13,15}$), 34.11 ($C_{17,18}$ or $C_{19,20}$), 20.37 ($C_{19,20}$ or $C_{17,18}$), 17.21 (C_{14}). CI-MS *m/z*: 382.3 (calcd. for $C_{24}H_{31}NO_3$ 381.2).



1

Benzyloxyamine of styrenic alcohol 2

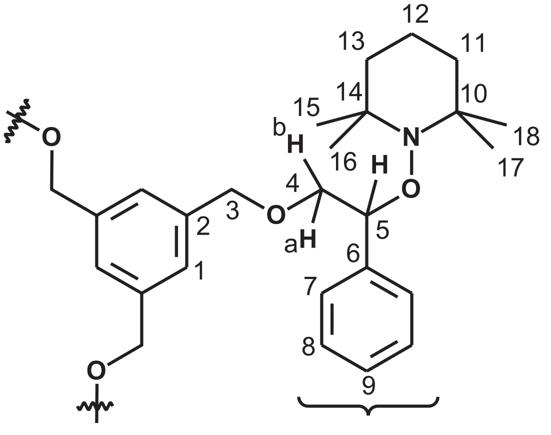
The reaction mixture consisting of ester **1** (4.0 g, 10 mmol) in ethanol (ca. 150 mL) and 2 mol L^{-1} KOH (25 mL) was heated under reflux for 3 h. After removal of ethanol on a rotary evaporator, the residue was dissolved in CH_2Cl_2 (100 mL), which was extracted with water (3 × 100 mL). The residual CH_2Cl_2 solution was dried over anhyd. $MgSO_4$. After removal of the solvent, the product was purified by flash column chromatography using CH_2Cl_2 as the eluant to give **2** as a light yellow oil (2.70 g, yield 97%). IR (neat, cm^{-1}): 3421–3302, 2930, 1739; 1721, 1606, 1458, 1360, 1248, 1125, 1027, 920, 762, 703. ^1H NMR ($CDCl_3$) δ: 7.43–7.32 (5H, m, H_{aryl}), 5.92 (1H, br s, H_{OH}), 1.64–1.46 (6H, m, $H_{8,9,10}$), 1.58, 1.39, 1.30, 1.22 (12H, br s, $H_{12,13,14,15}$). The signals for H_{1a}, H_{1b}, and H_2 could not be fully resolved, however, the ^{13}C NMR signals were in satisfactory agreement with the reported data (15) and the MS is also satisfactory. ^{13}C NMR ($CDCl_3$) δ: 138.31 (C_3), 127.72 (C_5), 127.27 (C_6), 126.17 (C_4), 83.02 (C_2), 69.05 (C_1), 61.04 (C_7 or C_{11}), 59.76 (C_7 or C_{11}), 39.78, 39.60 ($C_{8,10}$), 33.99, 32.45 ($C_{12,13}$ or $C_{14,15}$), 20.11, 19.79 ($C_{14,15}$ or $C_{12,13}$), 16.53 (C_9). CI-MS *m/z*: 278.2 (calcd. for $C_{17}H_{27}NO_2$ 277.20).



2

Williamson ether coupling of 2 and 1,3,5-tris(iodomethyl)benzene

A solution of alcohol **2** (2.50 g, 10 mmol) in dry THF (50 mL) in a RB flask fitted with a reflux condenser was treated with dry sodium hydride (1.10 g, 5 mmol) and the reaction mixture was stirred under argon at room temperature for 4 h. The iodo compound (1.25 g, 2.50 mmol) in dry THF (20 mL) was added slowly to the reaction mixture that was then heated at reflux for 24 h. On cooling, the resultant precipitate was filtered and the filtrate was evaporated to dryness. The residue in CH_2Cl_2 (100 mL), was washed with water (3 × 100 mL), and purified by flash column chromatography using ethyl acetate – hexanes – CH_2Cl_2 (1:3:6) as the eluant to give unimer I as a light yellow thick syrup (2.30 g, 97%). IR (neat, cm^{-1}): 2925, 2854, 1605, 1458, 1376, 1242, 1183, 957, 858, 761. ^{1}H NMR (CDCl$_3$) δ: 7.33–7.25 (15H, m, H$_{aryl}$), 6.78 (3H, s, H$_1$), 4.85 (3H, app t (overlapping d, d), J_{4b5} = 6.6, J_{4a5} = 5.1, H$_5$), 4.31 (6H, q, J_{H-H} = 12.3, H$_3$), 3.94 (3H, d, d, J_{4a4b} = 9.6, J_{4a5} = 5.1, H$_{4a}$), 3.64 (3H, d, d, J_{4a4b} = 9.6, J_{4b5} = 6.6, H$_{4b}$), 1.61–1.13 (18H, m, H$_{11,12,13}$), 1.33, 1.19, 1.05, 0.66 (36H, each br s, H$_{15,16,17,18}$). ^{13}C NMR (CDCl$_3$) δ: 141.91 (C$_2$), 138.28 (C$_6$), 127.80, 127.72 (C$_{7,8}$), 127.15 (C$_9$), 125.21 (C$_1$), 85.36 (C$_5$), 72.72 (C$_{3,4}$), 60.03 (C$_{10,14}$), 40.40 (C$_{11,13}$), 33.82 (C$_{15,16}$ or C$_{17,18}$), 20.26 (C$_{17,18}$ or C$_{15,16}$), 17.09 (C$_{12}$). HR-MS (FAB+) calcd. for $C_{60}H_{88}N_3O_6$: 946.667 7; found: 946.692 7. Anal. calcd. for $C_{60}H_{87}N_3O_6$ (%): C 76.15, H 9.27, N 4.44; found: C 76.47, H 9.27, N 4.47.

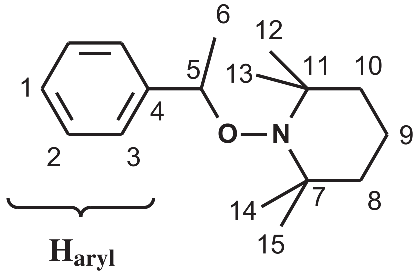


Unimer I

Unimer II

Illustrative synthesis of the benzyloxyamine of ethylbenzene (3 (X = H)) via the peroxyoxalate method

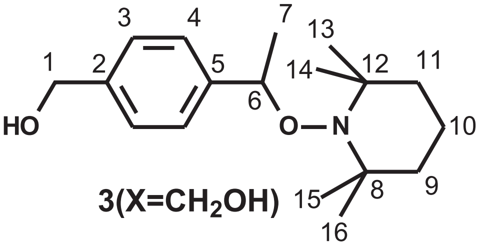
Di-*tert*-butylperoxyoxalate (2.21 g, 9.6 mmol), prepared by a modification of Bartlett's method (16) in 25 mL of ethylbenzene was treated with TEMPO (1.0 g, 6.4 mmol) and the mixture was stirred under argon at 35 °C. The red colour of the solution disappeared to give a light yellow solution within 30 min. Excess ethylbenzene was removed under reduced pressure at r.t. to give a viscous oil that solidified on standing in the refrigerator. The solid was repeatedly recrystallized from ethanol to provide the benzyloxyamine of 4-ethylbenzene (**3** (X = H)) (1.55 g, 93%) as colourless needles, mp 44 °C (lit. value (16) mp 44–46 °C). IR (KBr disk, cm^{-1}): 2977, 2936, 1461, 1366, 1283, 1244, 1218, 1126, 1064, 980, 927, 778, 699. ^{1}H NMR (CDCl$_3$) δ: 7.36–7.25 (5H, m, H$_{aryl}$), 4.82 (1H, q, J_{H-H} = 6.6, H$_5$), 1.52 (3H, d, J_{H-H} = 6.6 H$_6$), 1.42–1.28 (6H, m, H$_{8,9,10}$), 1.36, 1.21, 1.07, 0.700 (12H, each br s, H$_{12,13,14,15}$). ^{13}C NMR (CDCl$_3$) δ: 145.86 (C$_4$), 128.02 (C$_2$), 126.77 (C$_1$), 126.61 (C$_3$), 83.13 (C$_5$), 59.67 (C$_{7,11}$), 40.39 (C$_{8,10}$), 34.19 (C$_{12,13}$ or C$_{14,15}$), 23.58 (C$_6$), 20.32 (C$_{14,15}$ or C$_{12,13}$), 17.25 (C$_9$). CI-MS *m/z*: 262.3 (calcd. for $C_{17}H_{27}NO$ 261.2).



3(X=H)

Illustrative synthesis of the benzyloxyamine of 4-ethylbenzyl alcohol (3 (X = CH$_2$OH)) via Jacobson's method

The Jacobson reaction (11, 12) was carried out with 4-vinylbenzyl alcohol (2.0 g, 15 mmol), TEMPO (3.51 g, 23 mmol), [salen]MnCl (1.90 g, 3 mmol), di-*tert*-butyl peroxide (2.20 g, 15 mmol), sodium borohydride (1.14 g, 30 mmol) in toluene–ethanol (1:1) (300 mL) medium at r.t. for 30 h. Removal of solvent under vacuo, extraction (CH$_2$Cl$_2$), H$_2$O wash, drying (MgSO$_4$), followed by flash column chromatography (CH$_2$Cl$_2$ eluant) yielded **3** (X = CH$_2$OH) as a light yellow solid (2.20 g., 51%), mp 40 °C. IR (neat, cm^{-1}): 3326 (broad), 2932, 1457, 1365, 1250, 1199, 1128, 1055, 944, 829, 732. ^{1}H NMR (CDCl$_3$) δ: 7.33 (4H, s, H$_{3,4}$), 4.81 (1H, q, J_{H-H} = 6.6, H$_5$), 4.70 (2H, s, H$_1$), 2.20 (1H, br s, H$_{OH}$), 1.49 (3H, d, J_{H-H} = 6.9, H$_7$), 1.48–1.10 (6H, m, H$_{9,10,11}$), 1.33, 1.21, 1.07, 0.71 (12H, each br s, H$_{13,14,15,16}$). ^{13}C NMR (CDCl$_3$) δ: 144.95 (C$_5$), 138.99 (C$_2$), 126.45, 126.35 (C$_{3,4}$), 82.52 (C$_6$), 64.80 (C$_1$), 59.32(C$_{8,12}$), 39.94 (C$_{9,11}$), 34.08, 33.84 (C$_{13,14}$ or C$_{15,16}$), 23.34 (C$_7$), 19.99 (C$_{15,16}$ or C$_{13,14}$), 16.84 (C$_{10}$). CI-MS *m/z*: 292.3 (calcd. for $C_{18}H_{29}$NO2 291.2).



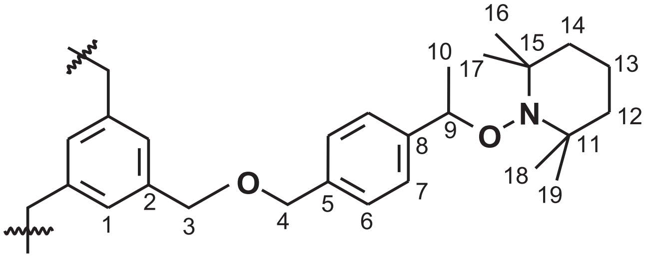
3(X=CH$_2$OH)

Silver-assisted S$_N$1 reaction for the formation of unimer II

Silver trifluoromethanesulfonate (silver triflate, $CF_3SO_3^-$ Ag^+) was employed for the etherification of **3** (X = CH$_2$OH) with the core (1,3,5-tris(bromoethyl)benzene).

A solution of the alcohol **3** (X = CH$_2$OH) (0.47 g, 1.60 mmol) and silver triflate (0.33 g, 1.60 mmol) in dichloromethane (10 mL) at 0 °C was stirred for 1 h following which the tris bromide (0.15 g, 0.42 mmol) was added and stirring was continued for another 6 h. The solution was then diluted with CH$_2$Cl$_2$ (20 mL), filtered through a plug of Celite, and the filtrate was washed with 1 mol L^{-1} HCl (50 mL), then satd. NaHCO$_3$ (50 mL), brine (50 mL), dried (MgSO$_4$), and finally concentrated by rotary evaporation. The crude product was purified by flash column chromatography using hexanes – ethyl acetate (3:1) as the eluant to give unimer II as a light yellow thick syrup (70 mg, 17%) and other complex by-products that could not be assigned. IR (neat): 2972, 2930, 2869, 1449, 1360, 1259, 1209, 1131, 1064, 1019, 935, 821, 680 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ: 7.33

(12H, s, $H_{6,7}$ and H_1), 4.80 (3H, q, $J_{\text{H-H}}$ = 6.6, H_9), 4.58 (12H, app. d, d, $H_{3,4}$), 1.70–1.30 (18H, m, $H_{12,13,14}$), 1.49 (12H, d, $J_{\text{H-H}}$ = 7.2, H_{10}), 1.32, 1.19, 1.05, 0.70 (36H, each br s, $H_{16,17,18,19}$). ^{13}C NMR ($CDCl_3$) δ: 145.29 (C_8), 138.73 (C_5), 136.53 (C_2), 128.00 ($C_{6,7}$), 126.60 (C_1), 82.87 (C_9), 72.17, 71.92 ($C_{3,4}$), 59.63 ($C_{11,15}$), 40.32 ($C_{12,14}$), 34.20 ($C_{16,17}$ or $C_{18,19}$), 23.57 (C_{10}), 20.31 ($C_{18,19}$ or $C_{16,17}$), 17.19 (C_{13}). FAB-HR-MS: $(M + H)^+$ calcd. for $C_{63}H_{94}N_3O_6$: 988.7143; found: 988.7141.



Unimer II

Unimer III

1,3,5-Tris(4′-nitrophenoxy)benzene (4-NO$_2$)

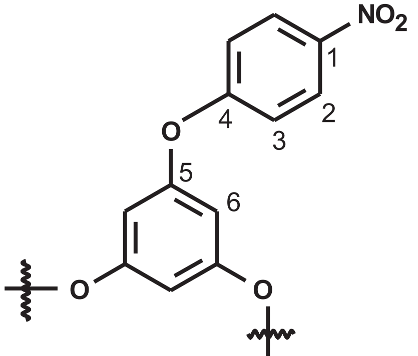
1,3,5-Tris(4′-nitrophenoxy)benzene (**4**-NO_2) was prepared via S_NAr displacement according to the method of Takeichi and Stille (17).

A mixture of 1,3,5-trihydroxybenzene dihydrate (phloroglucinol) (12.40 g, 76.50 mmol), 4-fluoronitrobenzene (24.4 mL, 230 mmol), potassium fluoride (26.70 g, 460.0 mmol), and 150 mL of DMSO was heated under reflux for 30 min. After cooling the precipitate that formed was filtered, washed with water (150 mL), and allowed to dry to give a crude product as a tan flaky solid. The supernatant of the initial filtrate on adding water (100 mL) gave more precipitate, which was filtered, washed with water (400 mL), and allowed to dry to give additional crude product. The combined crude products were recrystallized from ethyl acetate – charcoal and followed by chloroform–hexanes to give 1,3,5-tris(4′-nitrophenoxy)benzene (**4**-NO_2) as a creamy white solid (25.0 g, 50%), mp 203 to 204 °C (lit. value (17) mp 203.5–205.5 °C). IR (KBr disk, cm^{-1}): 3091, 2840, 2448, 1918, 1591, 1561, 1468, 1340, 1230, 1114, 994, 848, 741, 632. ^{1}H NMR ($CDCl_3$) δ: 8.27 (6H, d, $J_{\text{H-H}}$ ortho = 9.3, H_2), 7.15 (6H, d, $J_{\text{H-H}}$ ortho = 7.2, H_3), 6.67 (3H, s, H_6). ^{13}C NMR ($CDCl_3$) δ: 161.30 (C_4), 157.77 (C_5), 143.60 (C_1), 126.09 (C_2), 118.21 (C_3), 107.60 (C_6). HR-MS (EI) *m/z* calcd. for $C_{24}H_{15}N_3O_9$: 489.0801; found: 489.0819.

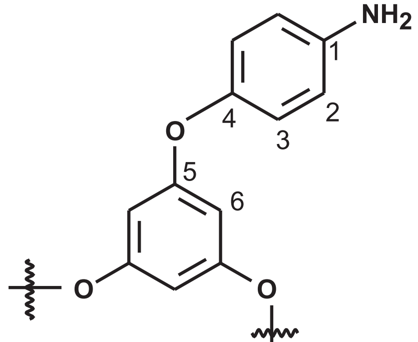
1,3,5-Tris(4′-aminophenoxy)benzene (4-NH$_2$)

Reduction of **4**-NO_2 was performed according to an experimental procedure adapted from the synthesis of 2,4-toluenediamine as described by Mahood and Schaffner (18).

To a stirred solution of **4**-NO_2 (8.0 g, 16 mmol) and Fe powder (8.10 g, 145 mmol) in 50% ethanol (100 mL) was added slowly HCl (0.6 mL concd. HCl in 10 mL of 50% ethanol). The reaction mixture was heated at reflux for 2 h and was then made alkaline to litmus with 15% aq. KOH. Without allowing the mixture to cool, the iron was filtered quickly and washed with 95% ethanol (2 × 50 mL). The solvent was removed by rotary evaporation and the residue was redissolved in chloroform (100 mL) and extracted with water (3 × 500 mL). The organic layer was dried ($MgSO_4$), filtered from the desiccant, evaporated to dryness, and further dried in vacuo for 48 h to give 1,3,5-tris(4′-aminophenoxy)benzene (**4**-NH_2) as a light purple solid (6.10 g, 94%), mp 88–90 °C (lit. value (18) mp 88 to 89 °C). IR (KBr disk, cm^{-1}): 3424, 3352, 3212 (NH_2), 1606, 1503, 1451, 1214 (C-O), 1113, 1003, 8.31 (C-N). ^{1}H NMR ($CDCl_3$) δ: 6.86 (6H, d, $J_{\text{H-H}}$ ortho = 8.7, H_3), 6.65 (6H, d, $J_{\text{H-H}}$ ortho = 8.7, H_2), 6.18 (3H, s, H_6), 3.67 (6H, br s, (H_{amino})). ^{13}C NMR ($CDCl_3$) δ: 160.77 (C_5), 147.84 (C_4), 142.90 (C_1), 121.23 (C_3), 116.17 (C_2), 99.97 (C_6). HR-MS (EI) *m/z* calcd. for $C_{24}H_{21}N_3O_3$: 399.1584; found: 399.1573.



4-NO$_2$



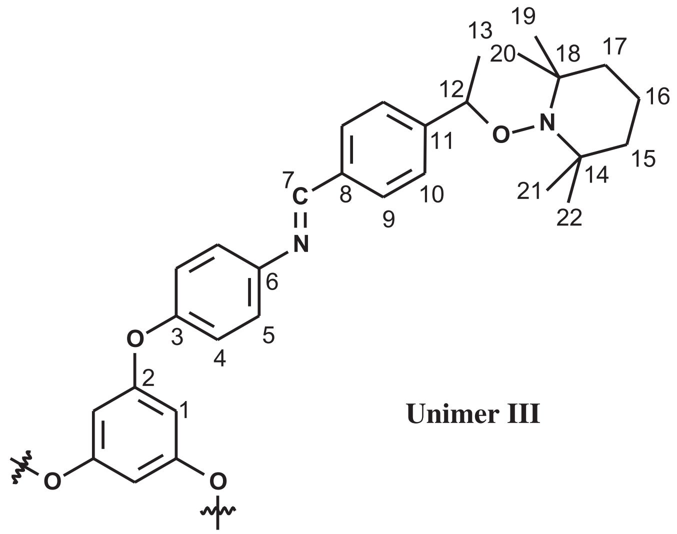
4-NH$_2$

Synthesis of the Schiff base adduct (unimer III)

Unimer III was prepared by the reaction of aldehyde **3** (X = CHO) with amine **4**-NH_2 via a method modified from Furniss et al. (19).

A solution of **3** (X = CHO) (0.60 g, 2.10 mmol) and **4**-NH_2 (0.25 g, 0.63 mmol) in 95% ethanol (10 mL) was stirred at reflux for 30 min after which water (3 mL) was added until cloudy and the solution was allowed to cool and induced to crystallize. The product was filtered, rinsed with cold aqueous ethanol, and purified by flash column chromatography using CH_2Cl_2 as the eluant to give unimer III, as a light yellow rubber-like solid (0.675 g, 85%). IR (KBr disk, cm^{-1}): 3435, 2969, 2928, 2869, 1614, 1497, 1453, 1366, 1218, 1121, 1064, 1003, 937, 836, 700. ^{1}H NMR ($CDCl_3$) δ: 8.47 (3H, s, H_7), 7.86 (6H, d, $J_{\text{H-H}}$ ortho = 8.1, H_9), 7.43 (6H, d, $J_{\text{H-H}}$ ortho = 8.1, H_{10}), 7.23 (6H, d, $J_{\text{H-H}}$

ortho = 8.7, H_5), 7.09 (6H, $J_{\text{H-H}}$ ortho = 8.7, H_4), 6.43 (3H, s, H_1), 4.85 (3H, q, $J_{\text{H-H}}$ = 6.6, H_{12}), 1.68–1.39 (18H, m, $H_{15,16,17}$), 1.52 (9H, d, $J_{\text{H-H}}$ = 6.6, H_{13}), 1.32, 1.20, 1.06, 0.69 (36H, each br s, $H_{19,20,21,22}$). ^{13}C NMR ($CDCl_3$) δ: 159.92 (C_7), 159.84 (C_2), 154.28 (C_8), 149.63 (C_{11}), 148.25 (C_6), 134.84 (C_3), 128.69 (C_9), 127.00 (C_{10}), 122.35 (C_5), 120.18 (C_4), 102.99 (C_1), 83.17 (C_{12}), 59.76 ($C_{14,18}$), 40.39 ($C_{15,17}$), 34.50 ($C_{19,20}$ or $C_{21,22}$), 23.64 (C_{13}), 20.37 ($C_{21,22}$ or $C_{19,20}$), 17.23 (C_{16}). ES-MS *m/z* calcd. for $C_{78}H_{96}N_6O_6$: 1213.7: found: 1214.3.



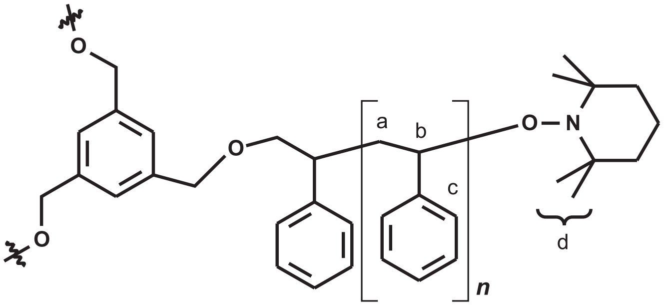
Unimer III

Synthesis of PS-3T1

SFRP 1 polymerisation of styrene (50 mL, 0.44 mol) using unimer I (0.36 g, 0.38 mmol) was carried out at 135 °C under nitrogen via bulk polymerisation (no solvent added) for 4 h. As the reaction proceeded, the clear solution became viscous over time. Intermediate samples (0.5 mL) were withdrawn at times 0.5 h, 1 h, 2 h, 3 h, and 4 h to follow the progress of polymerisation. Each intermediate sample was transferred into two small vials for thermal gravimetric analysis (TGA) and gel permeation chromatography (GPC) purposes. To determine conversion, the sample was transferred directly from the vial to the TGA apparatus. The second vial was evaporated to remove the excess styrene, diluted with THF (ca. 1 mL), and analyzed by GPC. Polymerisation was stopped after 4 h. The polymer was precipitated from methanol (500 mL), redissolved in dichloromethane (100 mL), and finally polystyrene with a terminal TEMPO group (**PS-3T1**) was isolated as a white powder, after drying in a vacuum oven at 50 °C for 12 h, yield 15.0 g. M_n = 34 200, M_n/M_w = 1.29.

Synthesis of PS-3T2

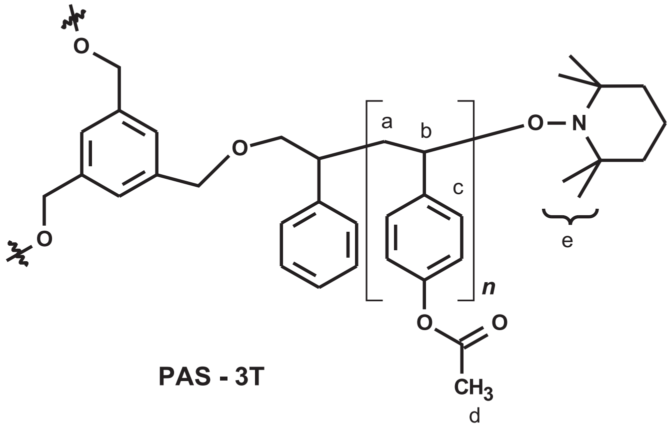
SFRP 2 polymerisation of styrene (25 mL, 0.22 mol) using unimer I (0.418 g, 0.500 0 mmol) was repeated in the identical manner as described above, forming **PS-3T2** as a white solid, 8.70 g. M_n = 12 700, M_n/M_w = 1.34.



PS - 3T1

Synthesis of PAS-3T

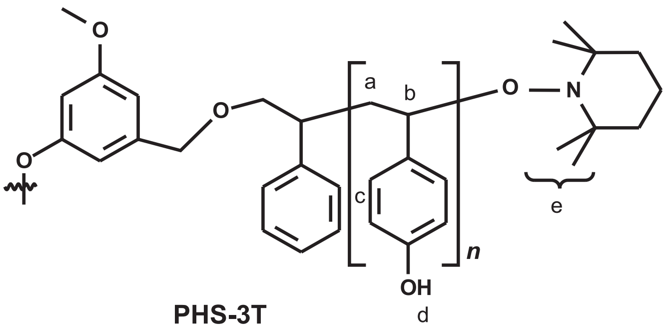
Bulk polymerisation of acetoxystyrene (25 mL, 0.164 mol) using unimer I (0.18 g, 0.38 mmol) was performed in an identical manner to the synthesis of **PS-3T1**. The product **PAS-3T** was obtained as a white powder (5.0 g). M_n = 21 100, M_n/M_w = 1.30.



PAS - 3T

Synthesis of PHS-3T

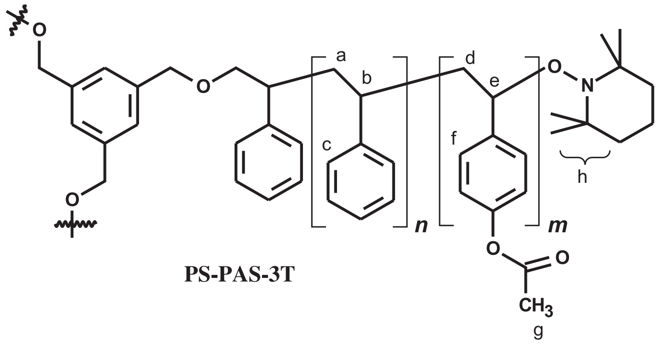
To a solution of **PAS-3T** (0.50 g) in methanol (20 mL) at reflux under nitrogen was added dropwise ammonium hydroxide (1.5 mL in 5 mL water). After the addition, heating of the reaction mixture was continued at reflux for 24 h. The reaction mixture was then cooled to room temperature, the polymer was isolated by precipitation in water (200 mL), filtered, and washed several times with water. The polymer was dried in a vacuum oven at 50 °C for 12 h to give star polyhydroxystyrene (**PHS-3T**) as a light yellow solid (0.3 g). Molecular weights and polydispersities of **PHS-3T** were estimated by GPC. M_n = 16 400, M_n/M_w = 1.23.



PHS-3T

Synthesis of block copolymer PS-PAS-3T

To a solution of acetoxystyrene (25.00 mL, 0.164 mmol) was added **PS-3T1** (10.0 g) and the reaction mixture was degassed under nitrogen for 30 min. The reaction mixture was then stirred and heated at 135 °C for 4 h. During this time the polymerisation mixture became progressively more viscous. The reaction mixture was cooled to room temperature, redissolved in dichloromethane (200 mL), and precipitated with methanol (1000 mL). The product was dried in a vacuum oven at 60 °C for 12 h to give **PS-PAS-3T** as a white powder (26.0 g). Molecular weights and polydispersities of **PS-PAS-3T** were estimated by GPC. M_n = 95 500, M_n/M_w = 1.21.



PS-PAS-3T

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