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Evaluating the Effect of Termination by Chain–Chain Coupling in Living Free-Radical Polymerizations

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A novel approach based on the reaction of multifunctional star polymers with chromophore-labelled linear polymers is presented for evaluating the extent of termination by chain–chain coupling during living free-radical polymerizations. A mixed initiating system consisting of an unlabelled, multifunctional initiator and an excess of a monofunctional alkoxyamine initiator containing a chromophore, such as pyrene, is used to initiate the living polymerization of vinyl monomers leading to a mixture of star and linear polymers. The occurrence of chain–chain coupling is readily identified and quantified by isolating the star polymer that is obtained and elucidating the level of incorporation of pyrene units by UV/vis spectroscopy. This allows the level of chain–chain coupling to be determined since the inclusion of pyrene into the star structure is a direct result of termination by radical coupling.

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The renaissance of research activity in the area of free-radical polymerizations has led to the development of various forms of living free-radical procedures (LFRP), with the three main techniques at the present being stable free-radical (nitroxide) polymerizations (SFRP),[1] atom-transfer radical polymerization (ATRP),[2] and radical addition, fragmentation, and transfer procedures (RAFT).[3] The advantages of living free-radical polymerizations, namely its versatility, synthetic ease, and compatibility with a wide variety of functional groups and macromolecular architectures, are key features driving this rapidly developing field. Interestingly, this renaissance has also coincided with the growing importance of well-defined macromolecules in the blossoming field of nanoscale science, for which many of the materials available from living free-radical procedures are perfectly suited.[4]

From the initial report[5] of using a multifunctional alkoxyamine initiator to prepare star polymers, the application of LFRP to the preparation of complex macromolecular architectures has blossomed and a myriad of different structures, ranging from stars,[6] hyperbranched,[7] comb,[8] to hybrid dendritic–linear macromolecules,[9] have been prepared. However, one feature that is typically neglected in the analysis and discussion of such structures is the occurrence of side reactions or termination processes that are typically associated with traditional free-radical chemistry. In LFRP these processes still occur, albeit at a reduced level. Therefore, to better understand the potential use of LFRP procedures for the preparation of complex macromolecular architectures and the associated level of possible impurities, it is important to evaluate the extent of these termination reactions. This is especially true for chain–chain coupling reactions since the effect of minor amounts of coupling is magnified due to the multifunctional nature of the initiators that are employed for the synthesis of these branched architectures. This manuscript describes the development of a general procedure for the identification and evaluation of chain–chain coupling reactions during living free-radical polymerizations.

To assess the level of chain–chain coupling reactions in LFRP, a novel approach has been developed based on the crossover reaction[10] between an unfunctionalized, multifunctional alkoxyamine initiator (1) and a functionalized, monoalkoxyamine initiator (2). As depicted schematically in Scheme 1, in the absence of radical–radical coupling reactions, polymerization of a vinyl monomer using both the dodeca-functionalized initiator (1) and the chromophore-labelled initiator (2) gives a mixture of a 16-arm star polymer (3) and a linear polymer (4). If crossover did not occur, only the linear polymer (4) would contain a single chromophore (F) at the chain end. However, if radical–radical coupling reactions do occur during the polymerization, a mixture of coupled products would be obtained, one of which would be the crossover derivative (5) in which the growing arms of the star polymer undergo coupling with functionalized linear chains.

As a result, a partially terminated product (5) is obtained in which at least one of the 16 arms of the star polymer has been terminated with a chromophore-labelled linear chain. Due to the molecular weight differences between the linear

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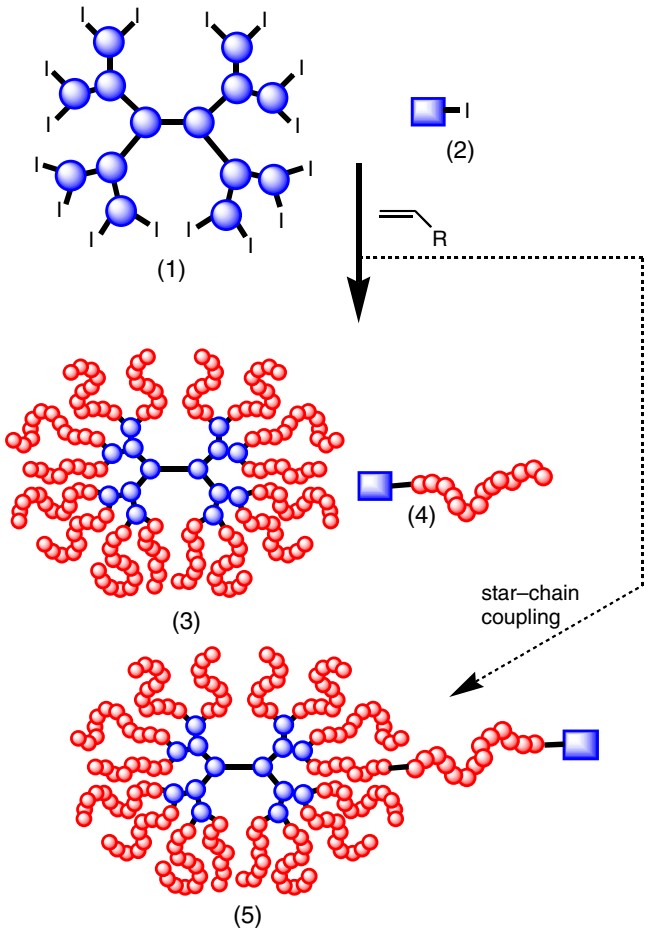
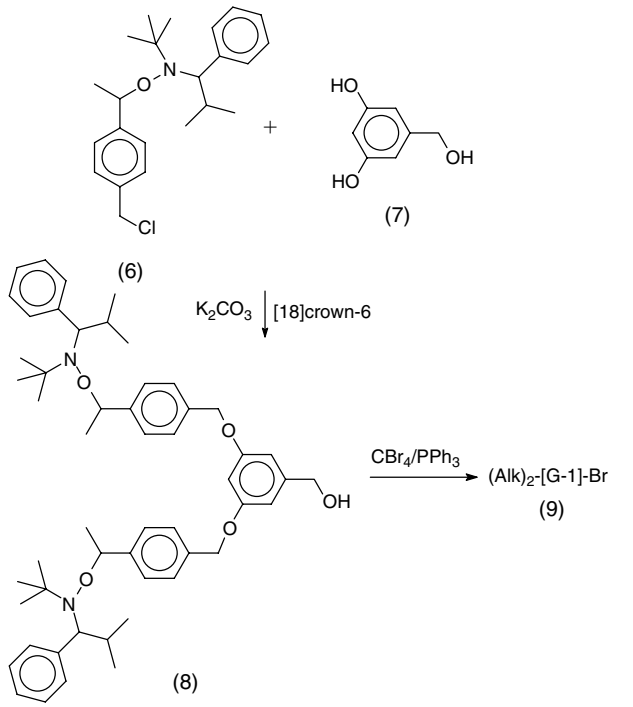


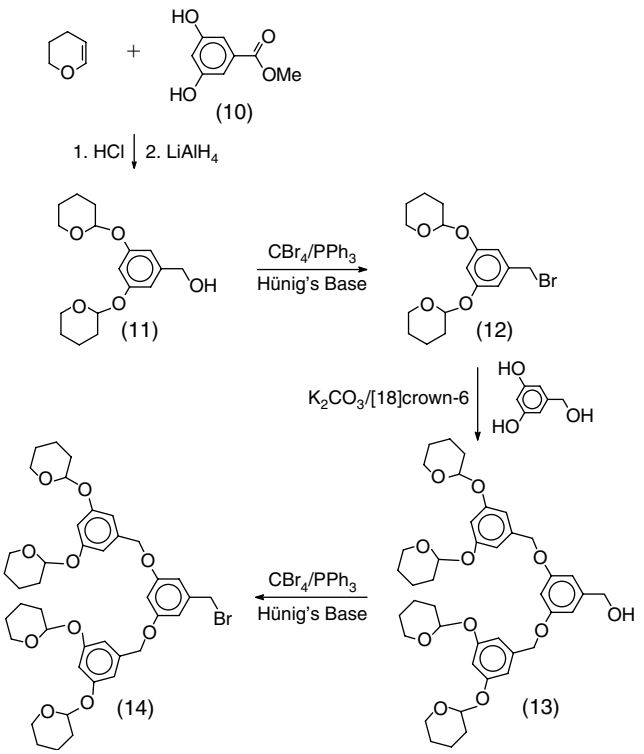
Scheme 1. Graphical representation of the strategy for detecting radical–radical coupling during living free-radical polymerization.

chains (4) and the star polymers (3) and (5), separation can be achieved by a number of different techniques and the level of incorporation of the chromophore in the star polymer can be determined by spectroscopy (Scheme 1).

The starting point for this strategy is, therefore, to use a multifunctional initiator such as (1), and it was initially envisaged that the appropriately functionalized Fréchet-type dendrimers would be employed due to the large body of literature concerning their synthesis and properties.[11] Employing a convergent approach[12] to the synthesis of multifunctional alkoxyamine initiators, the chloromethyl-substituted alkoxyamine (6) was treated with 3,5-dihydroxybenzyl alcohol (7) under Williamson etherification conditions to give the first generation dendritic fragment (8), which contains two alkoxyamine initiating centres. Bromination of (8) with carbon tetrabromide/triphenylphosphine gives the benzyl bromide $(Alk)_2$-[G-1]-Br (9) (Scheme 2). However, the yields obtained for the synthesis of (8) and (9) were poor (50–60%) and significantly below those normally obtained for Fréchet-type dendrimers. This trend of decreased yields accelerated for the second-generation derivatives, which precluded the use of a convergent approach for the synthesis of multifunctional dendritic alkoxyamines. One possible rationale for the lowered efficiency of dendrimer construction is the presence of the alkoxyamine groups at the chain ends, which leads to



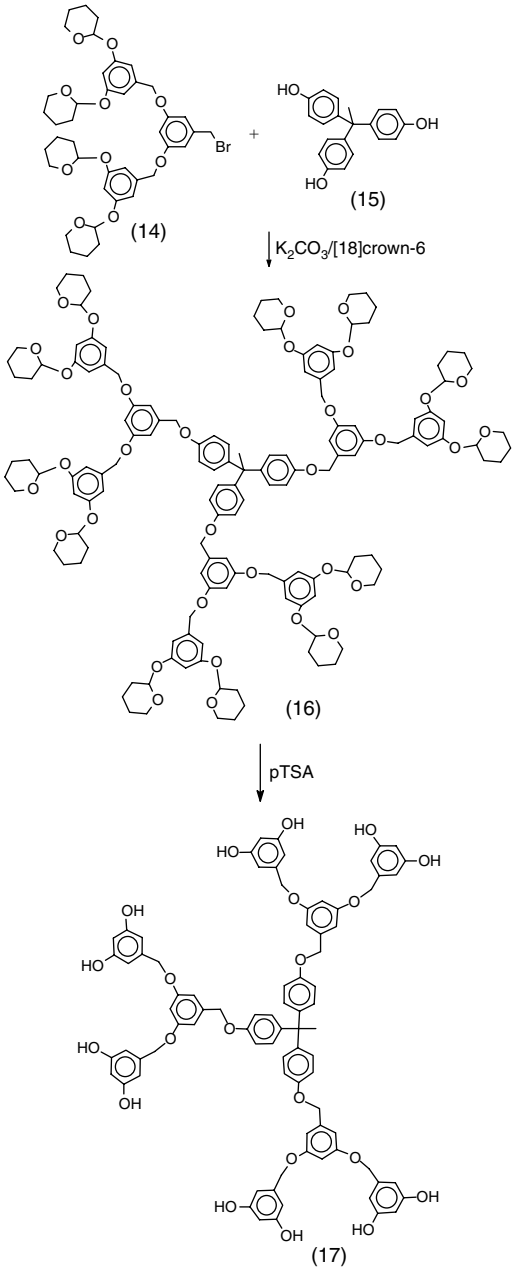
Scheme 2. Convergent synthesis of alkoxyamine-terminated Fréchet-type dendrimers.



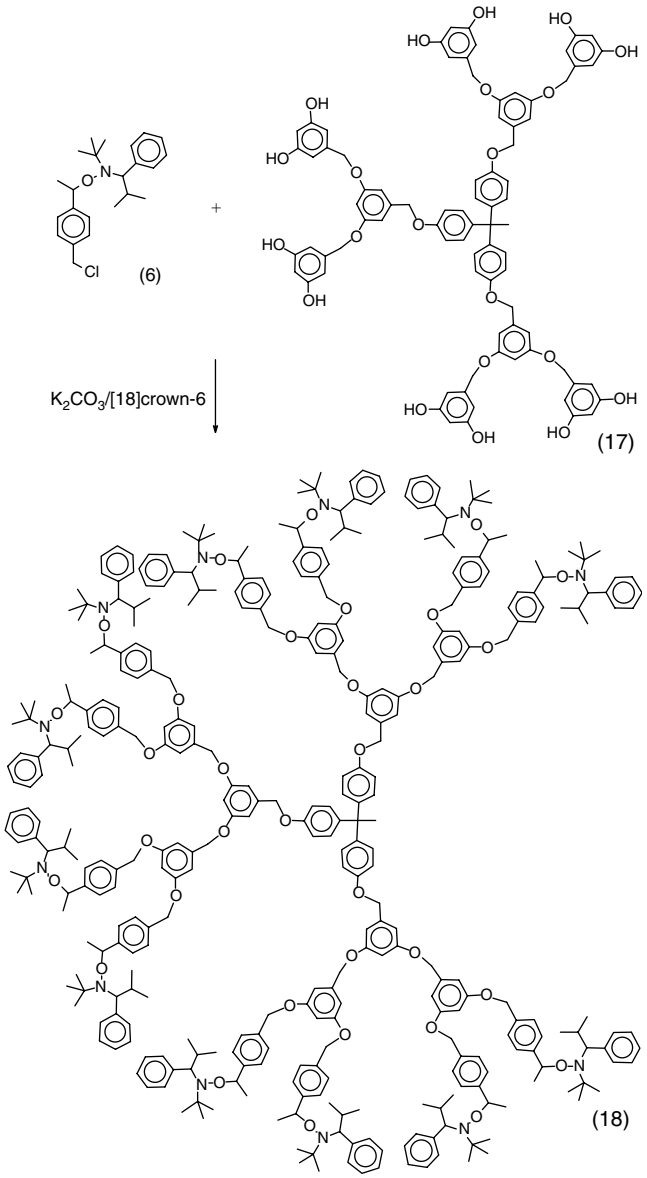
Scheme 3. Divergent synthesis of THP-terminated Fréchet-type dendritic fragments (13) and (14).

unwanted side reactions. As a result, a divergent approach[13] to the synthesis of alkoxyamine-substituted Fréchet-type dendrimers was developed, since this permits the alkoxyamine groups to be introduced in the final step of the synthesis.

For a divergent synthesis of Fréchet-type dendrimers to be successful, a critical feature is the choice of protecting



Scheme 4. Divergent synthesis of phenolic-terminated Fréchet-type dendrimer (17).

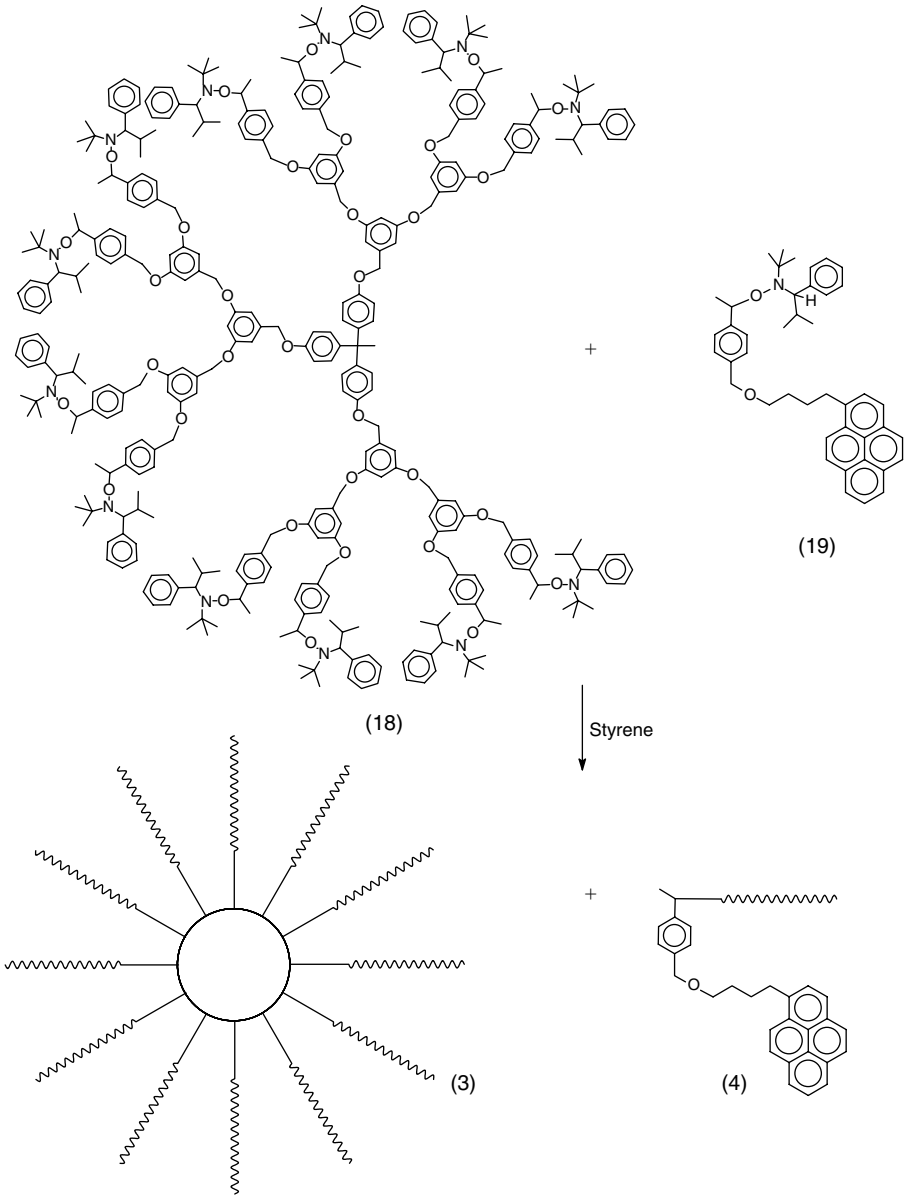


Scheme 5. Synthesis of alkoxyamine-functionalized polyether dendrimer (18).

group for the phenolic functionalities since it must be stable to the alkylation and bromination reactions used in construction of the dendrimer, and deprotection must occur cleanly and without any degradation of the dendritic benzyl ether bonds. Based on these criteria, the tetrahydropyranyl (THP) functionality was selected as the protecting group and introduced by acid-catalyzed addition of 3,4-dihydro-2*H*-pyran to methyl 3,5-dihydroxybenzoate (10), followed by lithium aluminum hydride reduction of the ester to give the benzyl alcohol (11) in high yield (Scheme 3). Bromination of (11) under standard (CBr_4/PPh_3) conditions gave poor yields of the benzyl bromide due to acid-catalyzed deprotection of the THP protecting groups. The addition of one equivalent of diisopropylethylamine (Hünig's base) to the reaction mixture was found to eliminate this side reaction and the desired benzyl bromide (12) was obtained in greater than 90% yield. Alkylation of 3,5-dihydroxybenzyl alcohol with (12) proved to be a facile process giving the second-generation alcohol (13), and bromination in the presence of Hünig's base afforded the bromide (14) with four THP-protected phenolic groups at the chain ends (Scheme 3).

Coupling of (14) with the triphenolic core (15) then gave the dendrimer (16), which could be deprotected by treatment with *p*-toluenesulfonic acid (pTSA) in a mixture of tetrahydrofuran and methanol, to give the dodecaphenol (17) (Scheme 4). Alkylation of dodecaphenol (17) with the chloromethyl-substituted alkoxyamine (6) proved to be a facile process which resulted in high yields of the initiator functionalized dendrimer (18). NMR and MALDI mass spectrometry confirmed that (18) had 12 alkoxyamine-initiating groups attached to a central dendritic core (Scheme 5).

With the unfunctionalized dendritic initiator (18), the precursor to the desired 12-arm star polymers, in hand,



Scheme 6. Polymerization of styrene initiated by a mixture of the dodeca-initiator (18) and the pyrene-functionalized initiator (19).

a functionalized alkoxyamine was prepared. The pyrene-functionalized alkoxyamine (19) was selected based on our previous work[14] on the determination of the relative incorporation of chain end functional groups.

In order to minimize the occurrence of coupling reactions between star polymers, an excess[15] of the functionalized alkoxyamine (19) was employed in the polymerization reaction of styrene (200 equivalents per alkoxyamine group), which was allowed to proceed to 84% conversion (Scheme 6). As can be seen in Figure 1, two symmetrical and narrow polydispersity peaks were observed eluting at 33.5 and 38.0 min. The former corresponds to the 12-arm star polymer (3) (M_n 195 000; PDI 1.08) and the latter to the pyrene-functionalized linear polymer (4) (M_n 18 000; PDI 1.06). Significantly, examination of the three-dimensional UV/vis–gel permeation chromatography (GPC) plot revealed absorbances at 320–360 nm for both peaks, which demonstrates that the pyrene functionality is incorporated into both the linear and star polymer structures. While this is expected for the linear polymer (4) due to the use of the functionalized initiator (19), the observation of pyrene absorbances for the star polymer is confirmation of an intermolecular coupling reaction between the growing linear polymer chain (4) and the 12-arm star polymer (3). As a result, the peak at 33.5 mL elution is an overlay of the unfunctionalized 12-arm star (3) and the pyrene-functionalized 12-arm star (5).

Separation of the mixture of (3) and (5) from the linear polymers was accomplished by preparative GPC due to the dramatic differences in molecular weight. The absence of pyrene-functionalized linear polymers (i.e. (4)) from the purified mixture of 12-arm stars was confirmed by rigorous multi-dimensional GPC analysis (combined RI and UV detectors), and the relative percentage of pyrene functionalized star (5) to unfunctionalized star (3) could then be calculated from the total pyrene absorbance. In the case of the above polymerization, which reached a conversion of

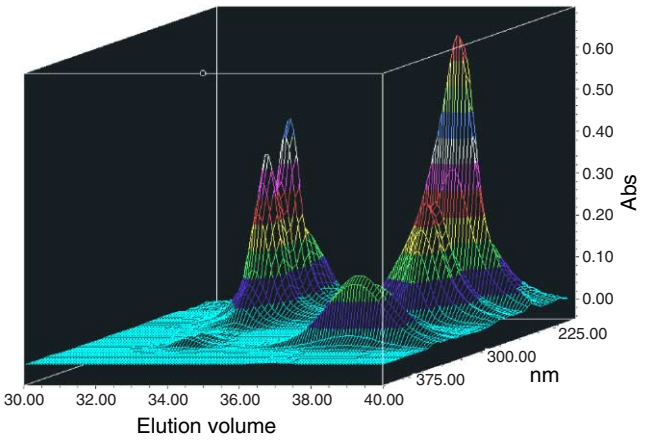


Fig. 1. Three-dimensional UV/vis–GPC plot (elution volume versus wavelength versus absorbance) for the polymerization of 200 equivalents of styrene at 120°C initiated by a mixture of (18) and (19).

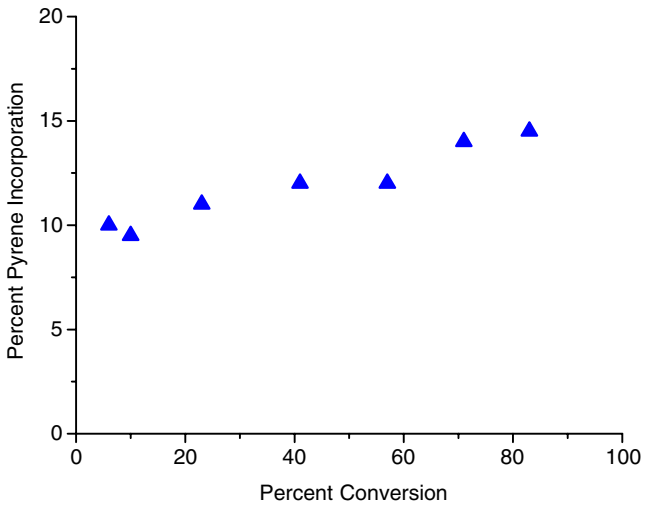


Fig. 2. Variation in the percent of pyrene incorporation with percent conversion for the polymerization of 200 equivalents of styrene at 120°C initiated by a mixture of (18) and (19).

84%, the level of pyrene incorporation was calculated to be 14%. If the assumption[16] is made that multiple coupling reactions giving rise to star polymers with more than one pyrene functionality are not significant, the extent of coupling for a single polymer chain or arm can be calculated (about 1.2%). The influence of conversion on this radical–radical coupling reaction was then examined by halting the polymerization at conversions ranging from 6 to 84%, isolating and purifying the star polymer, and subsequently determining the level of pyrene incorporation. As can be seen in Figure 2, this proved to be very instructive. A linear relationship going through the origin was not obtained; instead, a rapid increase in the level of pyrene incorporation was observed with approximately 10% incorporation being obtained after only 6% conversion. The level of incorporation then increased gradually to 14% at high conversions. This suggests that the majority of radical–radical coupling reactions occur early in the polymerization, which is fully consistent with the persistent radical effect proposed by Fischer.[17] In this theory, the homolysis of a dormant species (i.e. the

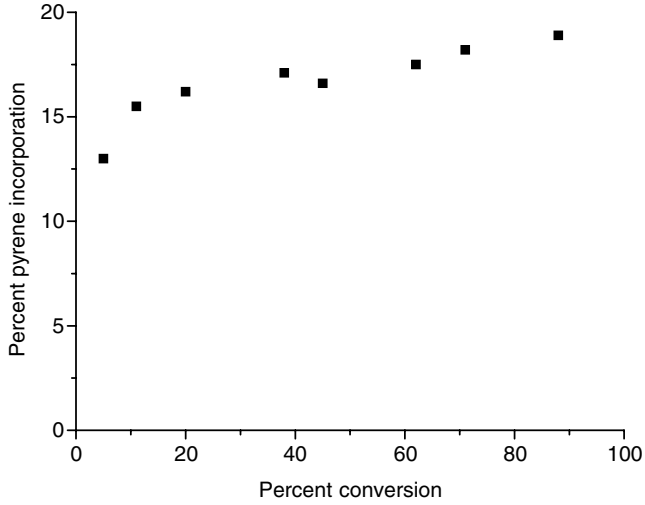


Fig. 3. Variation in the percent of pyrene incorporation with percent conversion for the polymerization of 200 equivalents of *n*-butyl acrylate at 120°C initiated by a mixture of (18) and (19).

alkoxyamine) gives a transient or propagating radical and a persistent radical (i.e. the nitroxide). While the persistent radical only undergoes reaction with the transient radical to regenerate the dormant species, the propagating radical can undergo reaction with monomer, the persistent radical, or itself. In the case of reaction with the persistent radical, or monomer and persistent radical, this leads to regeneration of the dormant species. However, reaction with another propagating radical (i.e. radical–radical coupling) leads to coupling and an overall reduction in the concentration of propagating radicals. As a result, the concentration of the persistent radical slowly increases, which gives rise to the persistent radical effect and leads to control of the polymerization process. Theoretical studies by Fischer et al.[18] have predicted this increase in the concentration of persistent radicals and associated decrease in concentration of transient radicals through radical–radical coupling to occur in the very early stages of the polymerization. This is also consistent with the expected decrease in the rate of the intermolecular coupling reactions as the degree of polymerization of the polymer chains increase due to steric effects.

To more fully understand this process, the polymerization of styrene in the presence of a mixture of (18) and (19) was repeated with 50 and 400 equivalents of styrene. In both cases, the level of pyrene incorporation was essentially the same at all conversions as that observed for reactions with 200 equivalents of styrene. These three experiments were then repeated with *n*-butyl acrylate as the monomer instead of styrene, and for these examples, 5 mol-% of the free nitroxide was added to control the polymerization and give a living system. As can be seen in Figure 3, the overall profile of the relationship between the level of pyrene incorporation and percent conversion for *n*-butyl acrylate is similar to that for styrene. The majority of coupling reactions occur at very low conversions, and above 10% conversion the level of pyrene incorporation increases at a much reduced rate. However, the most significant difference between the two monomer systems is the level of pyrene incorporation. For *n*-butyl acrylate

this varies from 15 to 20% over the conversion range (10–90%), which is about 50% higher than for the polymerization of styrene. It also correlates with approximately 1.7% of the polymer chains undergoing coupling. This suggests that while the overall profile of the radical–radical coupling reaction is independent of the length of the polymer chain above *DP* 50, the extent of the coupling reaction is dependent upon the nature of both the monomer and propagating polymer radicals.

In conclusion, a novel procedure based on cross coupling between functionalized linear chains and unfunctionalized star polymers has been developed to assess the extent of termination by radical–radical coupling in living free-radical polymerizations. For both styrene and *n*-butyl acrylate it was shown that the majority of termination by radical–radical coupling occurs early in the polymerization process, at conversions of less than 10%. While the overall relationship between termination and percent conversion is similar for both monomers, one significant difference is that the extent of termination is ca. 50% higher for *n*-butyl acrylate when compared with styrene (1.7% versus 1.2%). This low level of termination is consistent with the living character of the polymerization and the proven ability to prepare block and star copolymers. However, the values are not insignificant and demonstrate that termination by radical–radical coupling is an important event and should be taken into account when complex macromolecular architectures are prepared by living free-radical processes.

Experimental

General Methods

Commercial reagents were obtained from Aldrich and used without further purification. The synthesis of 2,2,5-trimethyl-3-(1-(4′-chloromethyl)phenylethoxy)-4-phenyl-3-azahexane was conducted using previously reported methods.[19] Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.24 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230–400 mesh, ASTM). NMR studies were performed on a Bruker AVANCE 400 FT-NMR spectrometer using deuterated solvents and the solvent peak as a reference. Gel permeation chromatography was performed in tetrahydrofuran (THF) on a Waters chromatograph equipped with four 5 μm Waters columns (300 × 7.7 mm) connected in series with increasing pore size (100, 1000, 100 000, 1 000 000 Å). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The polystyrene molecular weights were calculated relative to linear polystyrene standards, whereas the poly(*n*-butyl acrylate) molecular weights were calculated relative to poly(*n*-butyl acrylate) standards.

Methyl 3,5-Bis(tetrahydropyranyloxy)benzoate

To a stirred suspension of methyl 3,5-dihydroxybenzoate (40.0 g, 239 mmol) in dichloromethane (400 mL) was added 3,4-dihydro-2*H*-pyran (80.0 g, 952 mmol) followed by 12 drops of concentrated hydrochloric acid (38 wt-%). The reaction mixture was allowed to stir for 18 h and the solution was then concentrated under reduced pressure, loaded onto a silica column and purified by flash chromatography eluting with a mixture of hexane and acetone (20 : 1 volume ratio). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to give the ester as a white solid (92%) (Found: C, 64.4; H, 7.0; Calc. for $C_{18}H_{24}O_6$: C, 64.3; H, 7.2%). δ_H (400 MHz; [D_6]acetone; diastereomers) 1.54–2.10 (12 H, m), 3.60 (2 H, m), 3.80 (2 H, m), 3.90 (3 H, s), 5.50 (2 H, t), 7.00 (1 H, m), 7.30 (2 H, d, *J* 2.0). δ_C (400 MHz; [D_6]acetone; diastereomers) 19.7, 26.3, 31.3, 62.6, 97.5, 111.1, 111.6, 133.2, 159.4, 167.3.

3,5-Bis(tetrahydropyranyloxy)benzyl alcohol (11)

To a solution of methyl 3,5-bis(tetrahydropyranyloxy)benzoate (60.0 g, 178 mmol) in dry tetrahydrofuran (800 mL) was slowly added lithium aluminum hydride (20.0 g, 527 mmol). The gray mixture was allowed to stir at room temperature for 1 h and was then quenched with Baekstrom's reagent ($Na_2SO_4 \cdot 10H_2O$/celite, 1 : 1 wt ratio). Solids were removed from the reaction mixture by vacuum filtration through a coarse-grain glass frit and the clear, colourless solution was concentrated under vacuum. The benzyl alcohol (11) was isolated as a white solid after recrystallization from methanol (95%) (Found: C, 66.3; H, 7.9%. Calc. for $C_{17}H_{24}O_5$: C, 66.2; H, 7.8%). δ_H (400 MHz; [D_6]acetone; diastereomers) 1.54–2.10 (12 H, m), 3.55–3.60 (2 H, m), 3.82–3.94 (2 H, m), 4.60 (2 H, s), 5.50 (2 H, t), 6.61–6.65 (1 H, m), 6.71 (2 H, d, *J* 2.0). δ_H (400 MHz; [D_6]acetone; diastereomers) 19.9, 26.4, 31.5, 62.6, 65.1, 97.5, 104.9, 108.8, 146.0, 159.5.

3,5-Bis(tetrahydropyranyloxy)benzyl bromide (12)

To a solution of (11) (10.0 g, 32.4 mmol) in dichloromethane (200 mL) was added diisopropylethylamine (6.2 mL, 35 mmol), carbon tetrabromide (11.9 g, 35.8 mmol), and triphenylphosphine (9.40 g, 35.9 mmol). The mixture was stirred at room temperature for 1 h and quenched with deionized water (5 mL). The crude mixture was concentrated under vacuum and purified by flash chromatography eluting with a hexane/dichloromethane (4 : 1 volume ratio) solution that was gradually increased to dichloromethane and then dichloromethane/diethyl ether (10 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to yield the bromide (12) as a clear, slightly brown oil, which was used immediately (94%). δ_H (400 MHz; [D_6]acetone; diastereomers) 1.54–2.10 (12 H, m), 3.55–3.60 (2 H, m), 3.82–3.93 (2 H, m), 4.57 (2 H, s), 5.45 (2 H, t), 6.70–6.73 (1 H, m), 6.79 (2 H, d, *J* 2.0).

$(THP)_4$-[G-2]-OH (13)

To a solution of (12) (17.9 g, 48.1 mmol) and 3,5-dihydroxybenzyl alcohol (3.20 g, 23.0 mmol) in dry acetone (250 mL) was added [18]crown-6 (126 mg, 0.48 mmol) and anhydrous potassium carbonate (9.8 g, 72 mmol). The suspension was stirred vigorously under an argon atmosphere and refluxed for 24 h. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to dichloromethane/diethyl ether (10 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to give the second-generation dendrimer (13) as a white foam (93%) (Found: C, 68.1; H, 7.5%. Calc. for $C_{41}H_{52}O_{11}$: C, 68.3; H, 7.3%). δ_H (400 MHz; $CDCl_3$; diastereomers) 1.54–2.10 (24 H, m), 3.55–3.60 (4 H, m), 3.84–3.93 (4 H, m), 4.60 (2 H, s), 4.90 (12 H, s), 5.27–5.42 (4 H, m), 6.50 (1 H, m), 6.60 (2 H, d, *J* 2.0), 6.75 (2 H, m), 6.80 (4 H, d, *J* 2.0). δ_C ([D_6]acetone; diastereomers) 19.9, 26.4, 31.5, 62.6, 68.5, 70.6, 97.5, 101.5, 105.7, 106.3, 109.8, 140.8, 146.4, 159.7, 161.3.

$(THP)_4$-[G-2]-Br (14)

The same general procedure was employed as for the synthesis of (12) using the second-generation alcohol (13). Purification was performed using flash chromatography eluting first with light petroleum/dichloromethane (1 : 1), then dichloromethane, and finally dichloromethane/diethyl ether (10 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to yield the bromo derivative (14) as a colourless glass (90%) (Found: C, 63.0; H, 6.5%. Calc. for $C_{41}H_{51}BrO_{10}$: C, 62.8; H, 6.6%). δ_H (400 MHz; $CDCl_3$; diastereomers) 1.54–2.10 (24 H, m), 3.55–3.60 (4 H, m), 3.84–3.93 (4 H, m), 4.35 (2 H, s), 4.90 (12 H, s), 5.27–5.42 (4 H, m), 6.50 (1 H, m), 6.60 (2 H, d, *J* 2.0), 6.75 (2 H, m), 6.80 (4 H, d, *J* 2.0).

$(THP)_{12}$-($[G\text{-}2]$)$_3$-C (16)

To a solution of (14) (10.80 g, 13.83 mmol), 1,1,1-tris(4′-hydroxyphenyl)-ethane, and (15) (1.28 g, 4.19 mmol) in dry acetone (100 mL) was added [18]crown-6 (0.10 g, 0.37 mmol) and anhydrous potassium carbonate (5.0 g, 36 mmol). The suspension was stirred vigorously under an argon atmosphere and refluxed for 24 h. The crude product was purified by flash chromatography eluting with dichloromethane, gradually increasing to dichloromethane/diethyl ether (19 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to give the THP-protected dendrimer (16) as a white foam (67%) (Found: C, 71.3; H, 6.9%. Calc. for $C_{143}H_{168}O_{33}$: C, 71.1; H, 7.0%). δ_H (400 MHz; $CDCl_3$; diastereomers) 1.54–2.10 (72 H, m), 2.15 (3 H, s), 3.55–3.60 (12 H, m), 3.84–3.93 (12 H, m), 4.95 (18 H, s), 5.27–5.42 (12 H, m), 6.54–6.55 (3 H, m), 6.60 (6 H, d, *J* 2.0), 6.75 (6 H, m), 6.80 (12 H, d, *J* 2.0), 6.90 (6 H, d, *J* 8.0), 7.00 (6 H, d, *J* 8.0). δ_C ([D_6]acetone; diastereomers) 19.9, 26.4, 31.5, 62.6, 70.8, 97.5, 100.9, 105.7, 107.8, 110.0, 140.6, 141.3, 143.3, 158.1, 159.7, 161.4.

$(HO)_{12}$-($[G\text{-}2]$)$_3$-C (17)

To a solution of (16) (7.40 g, 3.12 mmol) in a mixture of tetrahydrofuran (100 mL) and methanol (50 mL) was added *p*-toluenesulfonic acid monohydrate (70 mg, 0.37 mmol). The reaction mixture was then allowed to stir at room temperature for 3 h before being quenched with sodium bicarbonate and purified by flash chromatography eluting with dichloromethane followed by dichloromethane/methanol (4 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to yield the dodecaphenol (17) as a colourless glass (61%) (Found: C, 67.5; H, 5.1%. Calc. for $C_{83}H_{72}O_{25}$: C, 67.8; H, 4.9%). δ_H (400 MHz, [D_4]MeOH) 2.05 (3 H, s), 4.85–4.86 (18 H, overlapping singlets), 6.18–6.19 (6 H, m), 6.35 (12 H, d, *J* 2.0), 6.49 (3 H, m), 6.61 (6 H, d, *J* 2.0), 6.78 (6 H, d, *J* 8.0), 6.92 (6 H, d, *J* 8.0). δ_C ([D_6]acetone) 31.3, 70.8, 101.4, 107.4, 115.3, 130.9, 141.0, 141.3, 143.3, 158.5, 160.0, 161.5.

General Procedure for the Alkylation of Phenol-Terminated Dendrimers with 2,2,5-Trimethyl-3-(1-(4′-chloromethyl)phenylethoxy)-4-phenyl-3-azahexane $(Alk)_{12}$-($[G\text{-}2]$)$_3$-C (18)

To a solution of (17) (1.30 g, 0.88 mmol) and the chloromethyl-substituted alkoxyamine (6) (4.57 g, 14.7 mmol) in dry acetone (50 mL) was added [18]crown-6 (0.10 g, 0.38 mmol) and potassium carbonate (4.0 g, 29 mmol). The suspension was stirred vigorously under an argon atmosphere and refluxed for 24 h. The reaction mixture was then cooled to room temperature, evaporated to dryness, partitioned between water (200 mL) and dichloromethane (200 mL), and the aqueous layer extracted with dichloromethane (2 × 100 mL). The combined organic extracts were then dried and evaporated to dryness. Purification of the crude product was performed using flash chromatography eluting with dichloromethane/diethyl ether (50 : 1). Fractions collected from flash chromatography were combined and the solvent was removed under vacuum to give the multifunctional alkoxyamine initiator (18) as a gummy solid (72%) (Found: C, 78.3; H, 8.3; N, 3.1%. Calc. for $C_{359}H_{444}N_{12}O_{37}$: C, 78.1; H, 8.1; N, 3.1%). δ_H (400 MHz; $CDCl_3$) 0.02 (36 H, d, *J* 6.5), 0.30 (36 H, d, *J* 6.5), 0.57 (108 H, s), 0.70 (36 H, d, *J* 6.5), 0.83 (108 H, s), 1.10 (36 H, d, *J* 6.5), 1.31 (36 H, d, *J* 6.5), 1.40 (36 H, d, *J* 6.5), 1.90 (3 H, s), 2.12–2.14 (12 H, m), 3.07–3.20 (12 H, 2 × d, *J* 12.0), 4.70–4.83 (78 H, m), 6.32–7.25 (75 H, m).

4-(4′-Pyrenebutoxymethyl)-2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (19)

4-Pyrene butanol (2.20 g, 8.03 mmol) was dissolved in dry THF (50 mL) under an argon atmosphere. Sodium hydride (200 mg, 8.41 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The chloromethyl alkoxyamine (6) (3.04 g, 8.10 mmol) was added and the reaction was refluxed 16 h under argon. The reaction mixture was then evaporated to dryness, extracted with dichloromethane, washed with water, dried, filtered, and concentrated. The crude product was purified by flash chromatography eluting with light petroleum/dichloromethane (8 : 2) to give the labelled derivative (19) as a light-yellow gum (84%) (Found: C, 84.6; H, 7.9; N, 2.5%. Calc. for $C_{43}H_{49}NO_2$: C, 84.4; H, 8.1; N, 2.3%). δ_H (400 MHz; $CDCl_3$; both diastereomers) 0.22 (3 H, d, *J* 6.5), 0.54 (3 H, d, *J* 6.5), 0.77 (9 H, s), 0.92 (3 H, d), 1.04 (9 H, s), 1.31 (3 H, d, *J* 6.30), 1.54 (3 H, d, *J* 7.0), 1.62 (3 H, d, *J* 6.80), 1.70 (2 H, 2 × m), 2.35 (2 H, 2 × m), 3.40 (4 H, 2 × m), 3.41 (1 H, d, *J* 10.8), 4.50 (4 H, d, *J* 7.5), 4.95 (2 H, 2 × q, *J* 6.5), 7.10–7.50 (18 H, m), 7.70–8.20 (18 H, m). δ_C (100 MHz; $CDCl_3$; both diastereomers) 21.2, 21.2, 22.0, 22.2, 23.2, 24.7, 28.3, 28.5, 29.9, 29.9, 31.7, 32.1, 33.3, 60.5, 60.6, 70.1, 70.3, 72.9, 72.9, 82.5, 83.4, 123.5, 124.7, 125.1, 125.2, 125.8, 126.3, 126.4, 126.6, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 128.7, 129.8, 131.0, 131.1, 131.5, 136.9, 137.6, 142.3, 142.5, 144.4, 145.1.

General Procedure for the Nitroxide-Mediated Polymerization of Styrene Using a Mixture of the Dendritic Initiator (18) and the Pyrene-Labelled Alkoxyamine (19)

A mixture of styrene (13.5 g, 130 mmol, 200 equivalents), the dodeca-initiator (18) (100 mg, 0.018 mmol), and the pyrene-labelled alkoxyamine (19) (265 mg, 0.435 mmol) were weighed into a vial that contained a magnetic stir bar. The vial was degassed by three freeze–pump–thaw cycles and sealed under argon. The sealed vials were heated at 120°C for an appropriate reaction time, dissolved in dichloromethane, and purified by precipitation in methanol (three times). The star polymer was obtained by prepratory GPC eluting with THF, and was analyzed by SEC, NMR, and UV/vis.

General Procedure for Nitroxide-Mediated Polymerization of Acrylates Using a Mixture of the Dendritic Initiator (18) and the Pyrene-Labelled Alkoxyamine (19)

A mixture of *n*-butyl acrylate (16.64 g, 130 mmol, 200 equivalents), the dodeca-initiator (18) (100 mg, 0.018 mmol), the pyrene-labelled alkoxyamine (19) (265 mg, 0.435 mmol), and the free nitroxide (8.5 mg, 0.033 mmol, 0.05 equivalents) were weighed into a vial that contained a magnetic stir bar. The vial was degassed by three freeze–pump–thaw cycles and sealed under argon. The sealed vials were heated at 120°C for an appropriate reaction time, dissolved in dichloromethane, and purified by precipitation in methanol (three times). The star polymer was isolated by preparatory GPC eluting with THF, and was analyzed by SEC, NMR, and UV/vis.

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[15] A 1 : 24 molar ratio of the dodeca-initiator (18) to the pyrene-labelled initiator (19) was employed. In terms of the ratio of alkoxyamine groups, this represents a 1 : 2 ratio of alkoxyamine groups for (18) (12 alkoxyamine groups per molecule) compared with (19) (1 alkoxyamine group per molecule.)

[16] While coupling of two or more linear chains to the star polymer leading to a multiply-functionalized star is statistically possible, the low occurrence of monofunctionalization makes the incorporation of two or more pyrene functionalities unlikely. Therefore, in the calculation of the relative percentage of pyrene functionalized star polymers only mono-addition was considered. Additionally, intramolecular termination between arms within the star polymer is not considered.

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