Communications to the Editor

Novel Starlike Poly(methyl methacrylate)s by Controlled Dendritic Free Radical Initiation

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Polymers derived from radical-initiated polymerizations are of significant importance in industrial processes, since the polymerization process is simple and applicable to a wide range of monomers. However, the control of molecular weights and molecular weight distributions in classical free radical polymerization is poor, due to radical coupling and chain transfer reactions of the growing radical species. This lack of control has limited the applicability of radical polymerization techniques for the preparation of well-defined molecular architectures. In contrast to the development of controlled ("living") anionic and cationic polymerizations, progress in controlled radical polymerization is relatively recent. These living free radical polymerization techniques are based on the reversible end capping of growing chains during polymerization. This mediates the reactivity and minimizes radical dimerization and disproportionation. In this regard, the use of sterically hindered nitroxides (e.g. 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO) provides considerable control in the polymerization of styrene and a variety of other functionalized monomers.[1−8] Another approach to living free radical polymerization, termed atom transfer radical polymerization (ATRP), was recently described by Sawamoto et al. and Matyjaszewski et al. This technique utilizes transition metal−ligand complexes in conjunction with an appropriate organic halide for the polymerization of methacrylates and other monomers. In recent years, various metal complexes and monomers have been described which yield controlled linear homo- and copolymers by the ATRP process.[9−17] Advances in controlled radical polymerization have presented opportunities for their use in the generation of well-defined polymeric molecular architectures.

We have described living ring opening polymerization (ROP) using polyfunctional dendritic and hyperbranched hydroxy functionalized initiators to produce controlled branched, star, hyperbranched and dendrimer-like poly-(ϵ-caprolactone)s (PCL).[18−20] These polymers have been used in combination with precondensed phenyl-, and methyl/phenyl/silsesquioxanes (SSQs) to produce organic/

inorganic hybrid materials with nanoscopic heterogeneous morphologies.[21] Unlike the corresponding linear polymers, the star and hyperbranched architectures are less prone to macroscopic phase separation during the matrix curing process. This can be attributed in part to the stronger interaction of the organic polymer with the SSQ matrix due to the increased number of end groups, abundant polymer functionality, and the limited mobility and low chain entanglements of the branched polymers. We now extend this synthetic approach to the preparation of highly branched starlike PMMA homo- and copolymers using ATRP polymerization techniques and dendritic initiators. These polymers are also attractive candidates for the preparation of nanoscopic polymer blends for the reasons described above. The controlled thermal degradation profiles of these materials also suggest their possible utility as porogens (pore generators) for the generation of porous materials from the corresponding inorganic/organic hybrids. Porous materials of this type are of interest as ultralow dielectric constant insulating materials.[21]

The dendritic 6- and 12-arm initiators **3** and **7** for use as ATRP initiators were prepared by esterification of hydroxy functionalized precursors with 2-bromo-2-methylpropionyl bromide. To simplify the synthesis of higher generation initiators, a carboxylic acid functionalized two-arm precursor **2** was synthesized from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and 2-bromo-2-methylpropionyl bromide. Using the AB₂ molecule **2** as a building block, the six-arm initiator **3** was synthesized from 1,1,1-tris(*p*-hydroxyphenyl)ethane **1** by esterification using dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) in methylene chloride.[22] After purification by flash column chromatography, the six-arm initiator was obtained in 69% yield. The 12-arm initiator **7**, i.e., the second generation dendrimer, was prepared similarly using the AB₂ monomer **2** and a six-arm hydroxyl functionalized precursor **6**. The six-arm precursor was prepared according to literature procedures.[23−25] The functionalized initiator **7** was obtained in 43% yield. Spectral data of both initators are in accordance with the suggested structures.[26] As an example, Figure 1A shows the ¹H NMR spectrum of the dendritic 12-arm initiator **7**. The polymerization of freshly vacuum distilled methyl methacrylate (MMA) was performed in bulk. The respective initiators and the catalyst, i.e., bis-(triphenylphosphine) nickel dibromide, were first weighed into a flame-dried round-bottom flask equipped with a three-way stopcock. Several cycles involving evacuation and subsequent purging with argon were conducted to remove most of the dissolved of oxygen. Finally the purified and degassed MMA monomer was added under argon using a syringe and the mixture was heated to 95 °C until the contents of the flask completely solidified. The polymer was then dissolved in THF and precipitated by addition to methanol.
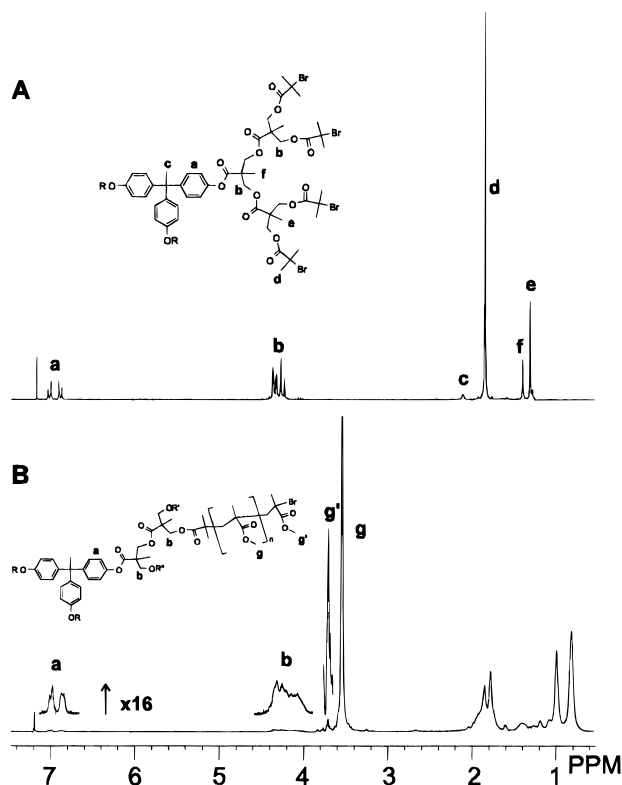
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Figure 1. ^{1}H NMR spectra of the dendritic 12-arm initiator **7** (A) and the corresponding 12-arm starlike PMMA **8** (B).

Scheme 1. Synthetic Route for the Preparation of Dendrimer-like Six-Arm Poly(methyl methacrylate)[a]

[a] Reaction conditions: (a) DCC/DPTS in CH_2Cl_2; (b) 95 °C, bis(triphenylphosphine) nickel dibromide (0.5 equiv with respect to initiating groups).

The target molecular weight for each polymer, calculated from the monomer-to-initiator ratio, was about 28 000. The measured number average molecular weights ($\bar{M}_n$) of the derived polymers were obtained both from ^{1}H NMR integration and from size exclusion chromatography (SEC). For the NMR analyses, the ratio of the integrated peak areas of the aromatic protons of the initiator core (**a** in Figure 1B) to that of the methyl ester side chains present in the polymer (**g**) was calculated. As can be seen in Table 1, the $\bar{M}_n$-values measured by NMR are in good agreement with the calculated values derived from the monomer/initiator ratio: 28 900 measured vs 28 500 calculated for the 6-arm PMMA and 26 500 measured vs 27 900 calculated for the 12-arm PMMA derivative. This suggests a degree of polymerization (DP) per arm of 48 for the six-arm PMMA branched polymer and 22 for the 12-arm example. SEC measurements based on calibration with linear polystyrene standards yield slightly lower $\bar{M}_n$-values. Since the shape of starlike polymers are certainly more globular in comparison with the random coil polystyrene standards, the molecular weights determined using SEC must be viewed with some caution. In fact, we have previously observed an increasing molecular weight discrepancy between SEC and NMR measurements for starlike PCLs with increasing number of arms as well.[27] Although the results from SEC may not reflect the accurate molecular masses because of the more globular shape of the polymers relative to the random coil polystyrene standards, this technique is a convenient method for determining the polydispersity of the synthesized star polymers. In accordance with the proposed living character of ATRP process, low polydispersities were measured for both polymers. These values ranged from 1.08 to 1.15 for the 6 and 12-arm polymers. This range represents data from multiple runs, whereas the
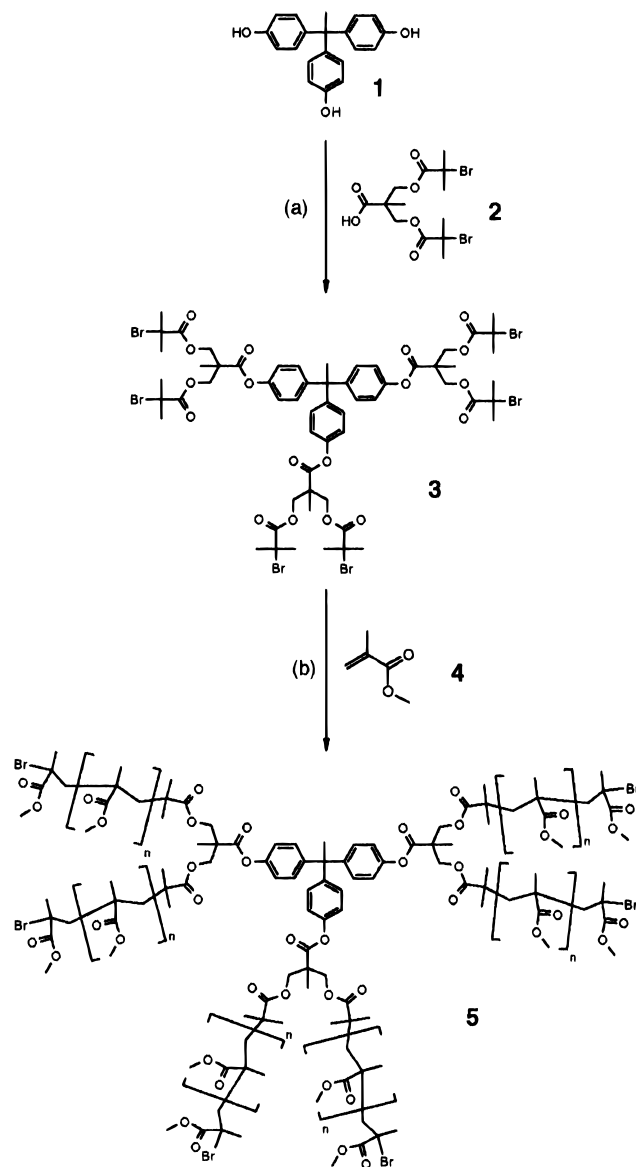
data in Table 1 refer to a representative run. The low polydispersity of the polymers strongly supports the conclusion that the polydispersity of the individual arms is low as well. Moreover, the SEC traces were symmetrical irrespective of the catalyst concentration (ranging from 0.5 equiv to stoichiometric) with no evidence of a high molecular weight tail that might be associated with intermolecular radical–radical coupling. However, the SEC data cannot completely rule out the possibility of intramolecular coupling (cyclization) particularly at high molecular weights.

In addition to the SEC analysis, the ^{1}H and ^{13}C NMR spectra of the starlike polymers were carefully analyzed. Figure 1B shows the ^{1}H NMR spectrum of the 12-arm polymer **8**. By comparison with the spectrum of the initiator **7**, the peaks at 6.9 and 4.2–4.4 ppm (**a** and **b** in Figure 1B) can be assigned to the initiator core of the starlike macromolecule. Unlike the signals for the aromatic protons, which are centered in both the initiator and the polymer at 6.9 ppm (**a**), the chemical shift

Scheme 2. Synthetic Route for the Preparation of Dendrimer-like Twelve-Arm Poly(methyl methacrylate)[a]
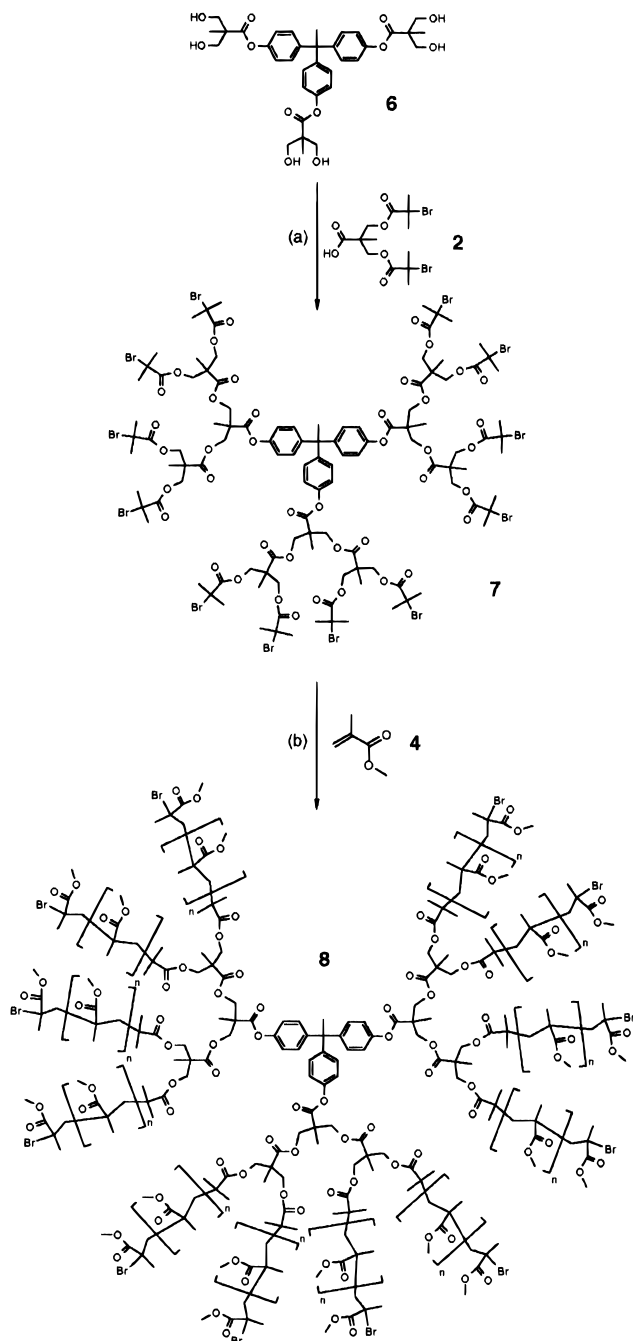

[a] Reaction conditions: (a) DCC/DPTS in CH_2Cl_2; (b) 95 °C, bis(triphenylphosphine)nickel dibromide (0.5 equiv with respect to initiating groups).

Table 1. Characteristics of Starlike Poly(methyl methacrylate)s

polymer	$\bar{M}_n$ (DP/arm)			$\bar{M}_n/\bar{M}_w$
	calcd[a]	¹H NMR[b]	SEC[c]	
6-arm **5**	28 500 (47.5)	28 900 (48)	25 200	1.12
12-arm **8**	27 900 (23)	26 500 (22)	20 000	1.08

[a] Calculated from the monomer/initiator ratio. [b] Calculated from the ratio of initiator aromatic protons to methyl ester groups in the polymer derived from ¹H NMR integration (protons **a** and **g** in Figure 1B). [c] GPC calibrated to polystyrene standards.

of the methylene groups (**b**) is slightly shifted in the polymer spectrum. Although the latter appears as an

AB-quartet around 4.2 ppm in both the first and second generation initiators, growth of the polymer chains causes a small upfield shift in the second generation methylene groups to about 4.1 ppm. In addition to the core initiator, the terminal-end groups of the starlike polymers can be assigned in the ¹H NMR spectrum as well. In addition to the strong resonance for the methoxycarbonyl groups of the repeat units PMMA (**g**) at 3.5 ppm, a small signal at 3.7 ppm (**g′**) appears in the spectrum. Consistent with the assignments of Sawamoto et al.[17,28] and Teyssié et al.,[16] this singlet is attributed to the methyl ester of the terminal bromo functionalized monomer unit. From the peak area ratio **a/g′**, 10.5 endgroups per star-polymer molecule were calculated. This number is reasonably close to theoretical value of 12, taking into account the integration error inherent to peak **g′**, due to overlapping peaks. A similar study on the six-arm polymer yields a calculated ratio of 5.7. These data provide tentative evidence that polymerization has occurred on all arms of the initiator. It also indicates, that intramolecular coupling (cyclization) if it happens at all occurs infrequently since this would decrease the number of functionalized endgroups. More conclusive evidence that all arms of the initiators reacted in the polymerization (at least for the six-arm derivative) can be gained from the ¹³C NMR spectra of the starlike polymers. No signals we observed around 67 ppm in the six-arm polymer spectrum unlike in the spectrum of the six-arm initiator. Signals in this region are assigned to the methylene carbons in the initiator. Polymerization causes a significant upfield shift of these carbon resonances. Extension of this approach to the ¹³C NMR spectra of the 12-arm derivative is more difficult since this initiator contains both first and second generation methylene carbons overlapping into a single signal centered at 67 ppm. Since only the chemical shift of the latter should be strongly affected by the proximate growing polymer chain, a residual signal from the inner core methylene groups around 67 ppm might be anticipated in the polymer. Consistently, a signal in this region is observed in the 12-arm polymer, although its relative intensity is greatly reduced as expected.

In conclusion, some novel poly(methyl methacrylate)s with starlike architectures have been synthesized by controlled radical polymerization starting from dendritic 6- and 12- arm multifunctional initiators. The initiators were obtained by coupling a bromo functionalized first generation dendron of bis-MPA to hydroxyl-functionalized precursors. The use of the ATRP technique allows the synthesis of branched and star polymers with accurate control of molecular weight and polydispersity. The living free radical character of the ATRP polymerization is supported by the remarkably low polydispersities of the polymers and the close correspondence between the calculated and measured molecular weights. NMR studies on the polymers were consistent with initiation occurring from all initiator arms. Additional results from two- and four-arm dendritic initiation studies as well as the preparation of starlike methyl methacrylate/hydroxyethyl methacrylate and other related copolymers will be described subsequently.[29]

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(26) Six-arm initiator **3**: ^{1}H NMR (CDCl$_3$) δ 1.47 (s, 9H, $-$CH$_3$), 1.92 (s, 39H, $-$C(Br)-CH$_3$), 2.13 (s, 3H, Ar$_3$$-C-CH_3$), 4.47 (q, 12H, $-$CH$_2$-), 7.05 (dd, 12 H, ArH); ^{13}C NMR (CDCl$_3$) δ 17.91, 30.7, 47.11, 51.69, 55.21, 66.32, 120.81, 129.78, 146.38, 148.58, 171.02, 171.14. Twelve-arm initiator **7**: ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 18H, $-$CH$_3$), 1.41 (s, 9H, $-$CH$_3$), 1.87 (s, 72H, $-$C(Br)-CH$_3$), 2.14 (3H, Ar$_3$$-C-CH_3$), 4.37 (q, 36H, $-$CH$_2$-), 7.03 (dd, 12 H, ArH); ^{13}C NMR (CDCl$_3$) δ 17.84, 17.95, 30.62, 46.85, 47.02, 55.33, 66.00, 120.70, 129.82, 146.37, 148.51, 170.72, 170.87, 171.67

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