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Notes

Investigation of the Initiation Behavior of a Dendritic 12-Arm Initiator in Atom Transfer Radical Polymerization

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Introduction

In recent years the polymer community has seen dramatic developments in the field of controlled radical polymerization techniques. Prominent examples include nitroxide-mediated,[1−8] transition-metal-mediated atom transfer radical polymerization (ATRP),[9−17] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[18] These techniques provide polymer chemists with convenient synthetic tools for the design and synthesis of well-defined, complex polymer architectures utilizing vinyl monomers such as styrenes, acrylates, and methacrylates.

Architectural control can be important in many polymer applications. This has been demonstrated recently for thermally labile polymers used as pore generators in the preparation of porous nanofoams.[19,20] As a result, we have become increasingly interested in the preparation of well-defined star homo- and copolymers with varying number of arms, particularly those which can be prepared utilizing ATRP techniques. With novel halogen-containing dendritic multiarm ATRP initiators containing up to 12 initiator sites (Figure 1), well-defined starlike PMMA with low polydispersities (1.08−1.2) and varying molecular weights (10 000−100 000 g/mol) could be obtained in bulk polymerization using dibromobis(triphenylphosphino)nickel(II) as the catalyst.[20,21] Size exclusion chromatography (SEC) traces of these polymers are symmetrical with no evidence of a high molecular weight fraction due to radical−radical coupling. Although these systems are apparently well controlled with respect to molecular weight and polydispersity, one of the most important questions associated with multiarm star polymers is whether the initiation is quantitative in a core-first approach. It was recently shown that the grafting of anionic polybutadiene onto a chlorosilane dendrimer containing 31 and 60 reactive functional groups, using an arm-first approach, resulted in an average number of arms of 29 and 54, respectively, due to steric effects.[22] This paper describes a detailed study on the initiation behavior of the dendritic 12-arm ATRP initiator **1** focusing on the actual number of initiated arms in the resulting multiarm polymer.

Several reports have recently appeared on the controlled preparation of star polymers via ATRP.[23−27] More radical−radical coupling is observed in solution polymerizations relative to those performed in bulk even at lower conversions presumably due to the increased mobility of the reactive chain ends in solution. Star polymers derived from multiarm ATRP initiators generally display low polydispersities and predictable molecular weights as calculated from the monomer/initiator ratio, in agreement with the controlled character of the polymerization. Gnanou reported the synthesis of starlike poly(styrene) in a bulk reaction using an octafunctional calix[8]arene intiator using CuBr/2,2′-bipyridine.[23] ^{1}H NMR studies and molecular weight analyses of the arms liberated by hydrolysis suggested that complete initiation had occurred. Related studies by Sawamoto[25] on the formation of star-branched PMMA derivatives from functionalized calixarene initiators produced similar results. A hexaphenyl-based initiator was studied by Robello for the ATRP of MMA with a CuBr/2,2′-bipyridine catalyst system.[26] Molecular weight analyses utilizing both SEC and light scattering suggested that an average number of 5−6 arms were initiated, and this depended on both the amount of catalyst employed and the molecular weight of the polymer. A kinetic approach for the determination of the number of initiated arms in a star system has also recently been described.[27]

Results and Discussion

The 12-arm ATRP dendritic initiator **1** used in our studies is shown in Figure 1. ^{1}H NMR spectroscopy, in principle, provides the most direct approach in determining whether all initiator sites react in the polymerization process. Unfortunately, the terminal methyl groups ($(CH_3)_2CBr-$) of the 12-arm initiator (1.83 ppm) are not useful in this analysis, since the intense proton signals of the growing PMMA polymer main chain (0.5−2 ppm) overlap this resonance. As discussed in detail in a previous paper, the terminal methoxycarbonyl end groups of the starlike polymers can often be detected in the ^{1}H NMR spectra.[21] For the 12-arm MMA polymer, a small singlet at 3.7 ppm appears slightly downfield from the intense singlet for the methoxycarbonyl groups of the MMA repeat units at 3.5 ppm. The number of arms can, in principle, be calculated from comparison of the integrated peak areas of the polymer end groups relative to the core signals although the integration errors may be significant (vide infra) due to weak signal strengths and spectral overlaps. Furthermore, any dehalogenation and/or radical coupling (intra- or intermolecular) would strongly affect this ratio. In the case of the 12-arm polymer, the number of

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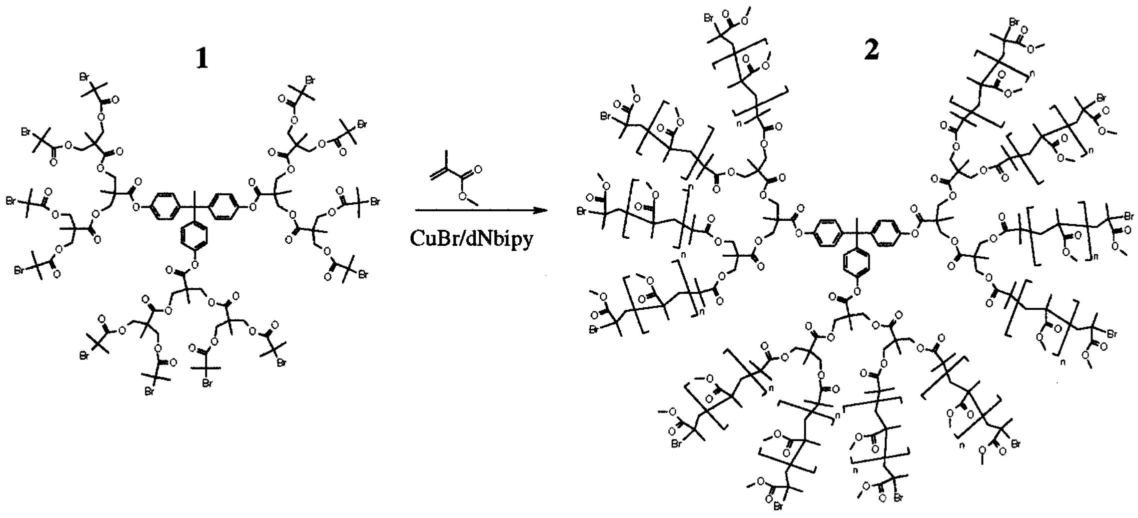

Figure 1. Preparation of the 12-arm MMA polymer from a 12-arm dendritic initiator.

halogenated end groups calculated from the ^{1}H NMR spectra was often lower than the theoretical value, and this ratio varied as a function of the polymerization conditions. To provide information on whether these observations are actually related to the presence of unreacted sites remaining on the initiator rather than to other processes such as thermal dehalogenation or radical–radical coupling (cyclization and/or dimerization), we synthesized polymers using partially deuterated monomer (MMA-d_5; $CD_2C(CD_3)CO_2CH_3$). Since the polymer main chain signals of the PMMA in the partially deuterated samples are now absent in the ^{1}H NMR spectrum of the star polymer, the resonance attributed to the terminal methyl groups of the initiator is directly observed. In addition, the number-average molecular weight of the polymer can still be calculated by ^{1}H NMR from the integrated peak areas of the methyl ester peak of the polymer side chains relative to the core signals.

Linear Model Polymer. To determine the chemical shift assignments of the initiator signals upon attachment of the polymer chain, a partially deuterated linear model polymer was synthesized from ethyl 2-bromo-2-methyl propionate following a literature procedure.[16] Figure 2A shows the respective ^{1}H NMR spectrum of the linear initiator. The resonance most susceptible to chemical shift changes caused by attachment of a polymer chain should be the methyl signal **c** at 1.9 ppm in the initiator. Figure 2B shows the spectrum of the polymer derived from the polymerization of MMA-d_5 (M_n: 9.0×10^3 g/mol; PDI 1.17). In agreement with the sites of deuteration in the monomer, just two polymer proton signals derived from the monomer are detected: the methyl ester peak **d** of the monomer unit and the methyl ester peak of the terminal monomer unit **d′**. The absence of polymer main chain signals allows us to follow the changes in the chemical shifts of the initiator group. As expected, the largest chemical shift change occurs for the signal attributed to the methyl groups **c** of the initiator. This signal shifts upfield from 1.9 ppm and results in a doublet structure centered at 1.1 ppm. The splitting is most likely due to polymer tacticity effects, since it is similar to that observed for the chain methyl groups in the PMMA itself. The peak at 1.6 ppm was identified as water since it disappears upon adding D_2O to the solution (Figure 2C).

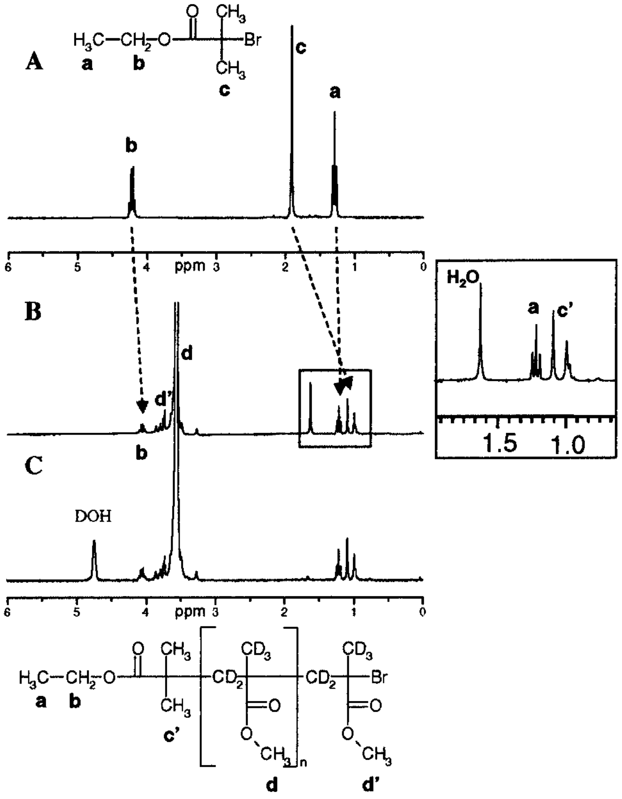

Figure 2. ^{1}H NMR spectra of a linear initiator (A) and linear PMMA-d_5 model polymer (B) before and after addition of D_2O (C). Bulk polymerization; 20% (w/w) catalyst (bis(triphenylphosphine)nickel dibromide) with respect to initiator, 95 °C.

12-Arm Deuterated Polymers. In the study of the initiation behavior of the 12-arm initiator **1**, we employed various reaction conditions, i.e., different catalyst systems and concentrations in bulk and solution polymerizations. Targeting a summed polymer arm molecular weight of 15 000 g/mol to facilitate the NMR analyses, we found that polymerization with purified CuBr/dNbipy is faster than for dibromobis(triphenylphosphino)nickel(II) under comparable conditions. The SEC traces of the polymers prepared in bulk using the nickel catalyst were always monomodal, even at high monomer conversions (>90%), with polydispersities below 1.2, whereas those of polymers derived from the more reactive copper catalysts often showed a high molecular

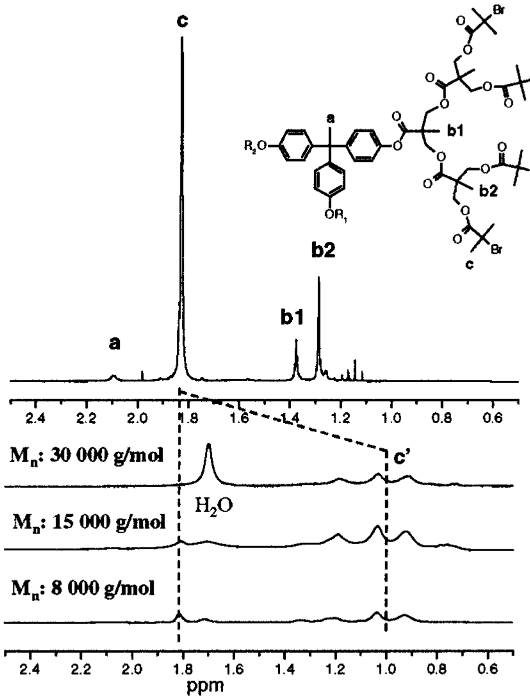

Figure 3. ^{1}H NMR spectra of 12-arm initiator and multiarm PMMA-d_5 polymers with varying molecular weights produced by solution polymerization. Solution polymerization (monomer/toluene 1:1), 50% (w/w) catalyst (CuBr/dNbipy) with respect to initiating units, 95 °C.

Table 1. Number of Arms Determined by ^{1}H NMR Spectroscopy (Partially Deuterated Monomer) in Solution and Bulk Polymerizations from the 12-Arm Dendritic Initiator 1

M_n[a] (g/mol)	no. of arms solution polymerization	no. of arms bulk polymerization
8 000	8	6
15 000	10	9−10
30 000	12	9−10
60 000	12	11−12

[a] Determined from integration of ^{1}H NMR signals of polymer methyl ester groups relative to initiator signals. The values are calculated for the 12-arm system based on the assumption of complete initiation at all sites (12) and do not include the initiator (3139 g/mol).

weight shoulder due to radical coupling at high conversions. The calculated number of initiated arms for the 15K polymer determined by ^{1}H NMR analyses *never* exceeded 10−11 regardless of the reaction conditions. We therefore prepared polymers of varying molecular weights to determine whether there is a minimum polymer molecular weight necessary for the initiation of all 12 arms of the dendritic initiator (vide infra). The reaction conditions for these experiments were chosen carefully using the more reactive CuBr/dNbipy system. Running the polymerization to high conversions (>90%) inevitably results in some end group coupling, particularly for the solution polymerizations, thus producing polymers with bimodal molecular weight distributions. While such radical coupling reduces the number of end groups relative to the core rendering a calculation of the number of arms using NMR end group analysis useless, such coupling should not affect the relevant chemical shifts of any brominated initiator sites remaining on the initiator core.

Figure 3 shows partial ^{1}H NMR spectra of the initiator **1** and three partially deuterated star-branched PMMAs with varying molecular weights synthesized by solution polymerization. In this region of the spectrum, the methyl groups **a** and **c** as well as **b1** and **b2** can be assigned. The latter groups can also be detected in the polymer spectra with a slight upfield shift as for the linear model polymer, the methyl peak **c′,** derived from the initiator can be used as a reference to determine the extent of initiation, i.e., the number of arms. The spectrum of the deuterated polymer derived from the 12-arm initiator is similar to linear model polymer. The initiator peak **c** results in a doublet shifted upfield to about 1 ppm (**c′**) upon attachment of the polymer chain to the initiator. The residual signal at the original position of the initiator methyl groups (1.85 ppm) suggested that not all initiator sites had initiated polymerization. This was further confirmed by dehalogenation of the polymer using tributyltin hydride according to a literature procedure.[28] In the polymer treated with tributyltin hydride, the signal **c**, tentatively assigned to those bromoalkyl groups that did not initiate, is not detected in the polymer spectrum. The number of uninitiated arms is more pronounced in the low molecular weight polymer ($M_n = 8 \times 10^3$ g/mol). Here the average degree of polymerization (DP$_n$) is calculated to be only 7 per arm. The number of arms calculated from the integrated areas of peak **c** relative to **c′** is about 8. Even in the polymer with a molecular weight of 1.5×10^4 g/mol (DP$_n$ = 13 per arm), a signal for uninitiated sites can still be detected. Spectral integration results in a calculated number of arms of 10 for this polymer. In the polymer with a molecular weight of 3.0×10^4 g/mol (DP$_n$ = 25 per arm), no residual signal at 1.85 ppm is detected. This suggests that for this molecular weight all initiator sites have initiated polymerization, and the calculated number of arms is 12. The results clearly suggest that a minimum molecular weight of the star polymer is required for complete initiation of all sites in the 12-arm initiator. This also implies that the polydispersity of the arms can be relatively high in the lower molecular weight polymers even if the polydispersity of the star polymer itself is low. This result corresponds well with the SEC results of the cleaved star polymer of Gnanou.[23] Our NMR results indicate that not all initiator sites on the multiarm initiator start the polymerization simultaneously. The reason for the staggered initiation for the 12-arm initiator might be due to steric and/or diffusional effects on the various rates. In a further study, we conducted the same series of polymerizations in bulk without solvent. In the bulk reaction the viscosity of the polymerization mixture increases more rapidly, eventually resulting in solidification of the reaction mixture at >90% monomer conversion: therefore, diffusional processes should be more affected in the bulk sample compared to the solution polymerization. We acknowledge, however, that steric effects may also be exacerbated in bulk due to the faster polymerization rates. Given that not all initiator sites on the multifunctional initiator start simultaneously, the chances for every individual site to initiate decreases as the polymerization rate increases. On the basis of this, we felt that the incomplete initiation effects should be more pronounced in the bulk polymerization and the minimum molecular weight to initiate all 12 arms should be higher. In bulk, the number of initiated arms also progressively increases with molecular weight as found in the solution polymerizations. Here, however, a very small residual signal at 1.85 ppm can be detected even for the polymer with a molecular weight of 6.0×10^4 g/mol, indicating incomplete initiation. The number of arms for this polymer is estimated to be 11−12 by integration, although these calculations become progressively less accurate as the polymer arm molecular weights increase. A comparison of the data for the solution and bulk polymerizations is shown in Table 1.

Conclusions

In conclusion, a detailed study of the initiation behavior of a dendritic 12-arm ATRP initiator was conducted. The results with partially deuterated monomer clearly show that the number of initiated arms increases with increasing molecular weight, and a minimum molecular weight is necessary to initiate all sites on the initiator. The minimum molecular weight necessary to ensure complete initiation depends on the reaction conditions. For this particular system, it requires a polymer molecular weight of about 3.0×10^4 g/mol in solution and at least 6.0×10^4 g/mol in a bulk polymerization. We suggest that the reason for the staggered initiation might be a combination of steric and diffusional effects. However, due to the plethora of ATRP catalysts and initiators available, every star polymer should be considered individually. These results show that a low polydispersity of multiarm polymers together with reasonable correspondence between the predicted and measured molecular weights of the polymers does not necessarily always ensure reaction at all initiator sites, particularly for initiators with a large number of arms. At lower monomer conversions (<50%) where end group coupling is minimized (i.e., the SEC traces are symmetrical and monomodal), the number of polymer arms calculated using either the polymer end groups (ratio of end groups/core) or the initiator groups (for deuterated monomer) leads to similar results.

Experimental Section

Size exclusion chromatography (SEC) was performed on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5um Waters columns (300 × 7.7 mm) connected in series in order of increasing pore sizes (100,1000, 10^5, and 10^6 Å) were used with THF as the solvent at room temperature and a flow rate of 1 mL/min. The GPC was calibrated with linear polystyrene standards. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM 250 (250 MHz) spectrometer. Dinonylpyridine (dNbipy) was synthesized according to a literature procedure.

Polymerization Procedures. *Bulk Polymerization Using Dibromobis(triphenylphosphino)nickel(II).* Into a Schlenk tube was placed 155 mg (0.05 mmol) of the 12-arm initiator 1, 50 mg (0.11 mmol) of the nickel catalyst, and 1.25 mL (1.395 g, 13.95 mmol) of distilled MMA. The contents of the flask were degassed by three vacuum/argon purge cycles and heated to 95 °C for 6 h. The solid contents of the flask were diluted with methylene chloride and precipitated into methanol. The solid was filtered and dried in a vacuum oven overnight: 1.4 g (90%), M_n 1.98×10^4, PDI 1.08 (SEC).

Bulk Polymerization Using CuBr Catalyst and MMA-d_5. Into a round-bottom flask equipped with a three-way stopcock were placed 170 mg (0. 050 mmol) of the 12-arm initiator 1, 30.8 mg (0.210 mmol) of CuBr, and 87.5 mg (0.210 mmol) of dNbipy. Most of the oxygen was removed by three evacuation/purge cycles with argon. Finally, 0.9 g (8 mmol) of MMA-d_5 which had been passed through a short column of neutral alumina to remove the inhibitor and thoroughly degassed was added, and the reaction was heated to 90 °C until the contents of the flask solidified (2 h). The reaction mixture was dissolved in methylene chloride and precipitated into methanol: yield 0.81 g (76%); M_n 1.5 × 104 g/mol (determined by ^{1}H NMR and calculated assuming 6 polymer chains/initiator molecule; the core molecule was not included in the calculation of molecular weight of the polymer); PDI 1.08 (SEC).

For the solution polymerizations, 2 equiv (v/v) of distilled toluene was used as the solvent. The amount of catalyst and ligand were increased (85 mg (0.59 mmol) of CuBr and 246 mg (0.590 mmol) of dNbipy) to maintain a similar catalyst concentration as in the bulk polymerizations. The reactions were run at 90 °C for 6−8 h, and the polymer worked up as described above. The number-average molecular weights of the PMMA chains were measured by ^{1}H NMR as described.

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