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One-Pot Hyperbranched Polymer Synthesis Mediated by Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization

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ABSTRACT: Reversible addition fragmentation chain transfer (RAFT) polymerization was used for the first time to produce poly(methyl methacrylate) hyperbranched polymers via the one-pot copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate, mediated by 2-(2-cyanopropyl) dithiobenzoate. Hyperbranched structures were characterized by ^{1}H NMR spectroscopy, size exclusion chromatography (SEC), and thermal analyses. Monomer conversions and molecular weight distributions of hyperbranched poly(methyl methacrylate) (PMMA) prepared via RAFT polymerization are much higher and much lower, respectively, than those of the analogous polymers prepared via other living polymerization systems. Furthermore, the living character of the RAFT process was used to polymerize styrene from hyperbranched PMMA precursors (macro chain-transfer agent, macroCTA) and to produce starlike structures with hyperbranched PMMA as the core and polystyrene as the arms. DSC and SEC analyses support the observations made regarding the production of these novel architectures.

Introduction

Dendrimers have attracted much interest in the past 10 years,[1–3] mainly due to their unusual, globular, and perfectly branched structures. Well-defined architectures, high numbers of functional groups on their surface, excellent solubility in a vast range of solvents, and very low viscosity make dendrimers good candidates for a wide range of applications, from viscosity modifiers to catalyst supports and drug carriers. The production of dendrimers, however, requires multistep syntheses, with drastic purifications between each step, making it a costly and time-consuming process. Hyperbranched polymers, in contrast, are often far easier to prepare under less drastic reaction conditions. Although they have less perfect branching structures than dendrimers, such systems retain high degrees of functionality, have improved solubility and low viscosity, and therefore provide a cheaper alternative to dendrimers for applications such as resin modification, encapsulation, polymeric liquid crystals, pharmaceutical use, catalysis, and electroluminescent devices. The creation and development of highly branched macromolecules with well-defined architectures via one-step processes is well documented in the literature, see for instance refs 4–6.

Most hyperbranched polymers are synthesized by step-growth polymerization via polycondensation of AB_x monomers. Here, A and B are the two functionalities that can react with each other but not with themselves. In an AB_2 monomer system, the branching is controlled by statistics and only reaches around 50%, far from the 100% usually achieved with dendrimers. Furthermore, as there is no control over size and structure, hyperbranched polymers show broad molar mass distributions. Moreover, facile routes to produce hyperbranched polymers via addition polymerization are very rare.[7] Frechet et al.[8] first reported the self-condensing vinyl polymerization (SCVP) process, where a vinyl monomer presents a second functional group that is capable of initiating the polymerization of other vinyl groups. Frechet's group initially used "living cationic" propagation, and have now extended their technique to include "group transfer" and "living free-radical" polymerizations.[9] Matyjaszewski[10] applied the principle of SCVP to copper-mediated living radical polymerization, in which the vinyl monomer possesses a second reactive group, such as a halogen atom, that can be reversibly activated and deactivated and, therefore, mediate living polymerization in the presence of a catalyst based on copper(I). Propagation can take place at either the double bond or after the initiation of the halogen functionality, resulting in branching points and eventually in hyperbranched polymers. However, this process is difficult to exploit industrially, as it requires expensive, tailored vinyl monomers with specific functional groups that require complex syntheses and the polymerizations need to be stopped at low conversions.

Sherrington and co-workers have devoted considerable study to the development of facile, versatile, and cost-effective routes to the synthesis of branched or hyperbranched polymers. Their strategy involves the conventional free radical polymerization of a vinyl monomer in the presence of a multifunctional vinyl comonomer.[7,11–15] Using mercaptans as chain-transfer agents to prevent cross-linking, they synthesized branched (meth)acrylic copolymers at high conversion, via a one-step process, by copolymerizing MMA with tripropylene glycol diacrylate.[7] They have also developed both branched gel-type poly(styrene-*co*-divinylbenzene)s and branched macroporous poly(styrene-*co*-divinylbenzene)s with a facile one-pot suspension polymerization.[12] They have widened their study by applying various multifunctional monomers to make branched methacrylate copolymers. This approach caused them to investigate the effect of multifunctional monomer functionality on

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chain architectures and polymers properties. For instance, branched poly(methyl methacrylate)s have been prepared by employing free-radical solution polymerization with ethylene glycol dimethacrylate (EGDMA) as a branching comonomer and dodecanethiol (DDT) as the chain-transfer agent.[11] Besides using the conventional chain-transfer agent in the synthesis of branched polymers, Sherrington's group, in collaboration with Armes' group, recently applied copper-mediated living radical polymerization (LRP) and group transfer polymerization (GTP) to the synthesis of soluble branched polymers in facile one-pot reactions.[13]

A striking observation from all of the investigations described above is that, although many specialized synthesis techniques have been used in preparing hyperbranched polymers, reversible addition fragmentation chain-transfer (RAFT) and macromolecular architecture design via interchange of xanthates (MADIX) polymerizations have never been investigated for such purposes, despite these being the most versatile of the LRP techniques. RAFT and MADIX polymerizations rely on the process of degenerative transfer of radical species to dithioester compounds (chain-transfer agent, CTA), as reported for the first time by Zard and co-workers in 1988.[16] The use of this process in a classic free-radical polymerization system (monomer + initiator) led to the development of the RAFT and MADIX processes in which the transfer of the CTA between growing radical chains, present at very low concentration, and dormant polymer chains, present at higher concentration (3 or 4 orders of magnitude), regulates the growth of the molecular weight and limits the termination reactions.[17−19] RAFT and MADIX have been demonstrated to control the living polymerization of a variety of monomers over a wide range of temperatures (25−120 °C) and under various reaction conditions (emulsion, bulk, solution polymerization) to produce a variety of polymeric architectures and materials. However, only two groups have reported the use of RAFT to generate cross-linked gel[20] or hyperbranched polymers.[21] Therefore, both RAFT and MADIX appear to be the techniques of choice for the production of hyperbranched polymers, via a living polymerization technique, in an industrially viable process.

In this article, we investigate the use of RAFT polymerization to produce hyperbranched PMMA in a one-pot reaction. The use of a chain-transfer agents gives the opportunity to assess with great accuracy the hyperbranched structures via ^{1}H NMR spectroscopy. The polymers were studied via NMR, size exclusion chromatography (SEC), and thermal analyses. Finally, the livingness of the RAFT process is used to generate novel architectures, namely hyperbranched-core star copolymers.

Experimental Section

Materials. All monomers, solvents, and other reagents were purchased from Aldrich at the highest purity available and used as received unless otherwise stated. methyl methacrylate (MMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), and styrene(99%) were filtered before use through an activated basic alumina (Brockmann I) column to remove radical inhibitors. Azobis(isobutyronitrile) (AIBN, 99%) was recrystallized twice from chloroform−methanol. 2-2′-cyanopropyl dithiobenzoate (CPDB) was synthesized following a previously reported preparation.[22]

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were recorded on a 400 MHz Bruker UltraShield spectrometer with $CDCl_3$ as the solvent and reference.

Table 1. Molar Ratios for the Synthesis of Hyperbranched Poly(methyl methacrylate) (PMMA) of Chain-Transfer Agent (CTA), Methyl Methacrylate (MMA), Ethylene Glycol Dimethacrylate (EGDMA), and Azobis(isobutyronitrile) (AIBN)

	molar ratios			
series	CTA	MMA	EGDMA	AIBN
F1	5.04	100	5.85	0.50
F2	3.00	100	5.85	0.30

Size Exclusion Chromatography. Molecular weight and molecular weight distributions were determined by size exclusion chromatography (SEC) at ambient temperature using a system equipped with a Polymer Laboratories 5.0-μm-bead-size guard column (50 mm × 7.5 mm) and two Polymer Laboratories 5.0-μm MIXED-C columns (molecular weight range of 2 000 000−500 g/mol) with both the differential refractive index detector (Shodex, RI-101) and UV detector (wavelength set at 256 nm for styrene analyses). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}, and toluene as a flow rate marker. Both the PMMA and PS with a MW range of 1 944 000−1020 g/mol, and 7 500 000−580 g/mol, respectively, were used for calibrations.

Differential Scanning Calorimetry. The glass transition temperatures (T_g's) of the prepared branched polymers were determined using a TA Instruments DSC 2010. The heating rate was set at 10 °C min^{-1} from room temperature to 450 °C. Nitrogen was used as an inert gas at a flow rate of 200 cm^3 min^{-1}. The sample weight used was in the range of 3 mg. The instrument was calibrated using gallium, indium, and zinc to cover the temperature range 0−100, 100−250, and 250−500 °C, respectively. T_g's were calculated using the instrument inbuilt software package TA Instruments Thermal Advantage.

Syntheses of Hyperbranched PMMAs via RAFT Polymerization. Two series of hyperbranched polymers were designed, as illustrated by Table 1. For the ratio CPDB/MMA/EGDMA/AIBN = 3:100:5.85:0.3, CPDB (660 mg, 3.0×10^{-3} mol), MMA (10.0 g, 0.10 mol), EGDMA (1.15 g, 5.8×10^{-3} mol), and AIBN (49.0 mg, 0.3×10^{-3} mol) were added to a solution of dried toluene (40.0 g), and 8 g of this solution was sampled in six 10-mL test tubes. Each tube was capped with a rubber septum, placed in an ice bath, and flushed with nitrogen for 10 min to remove oxygen. Finally, each tube was placed in a water bath (60 °C) and removed after a predetermined time. The resultant products were analyzed by ^{1}H NMR to establish the monomer conversions. The molecular weight and molecular weight distributions were determined by SEC. To acquire information on chain structures and on the thermal properties of the hyperbranched polymers, the products were precipitated in hexane and analyzed by ^{1}H NMR and DSC. Samples were taken after 8 h (29.5%, M_n = 2800 g/mol, M_w = 4200 g/mol, PDI = 1.52, 45% branching), 24 h (72.7%, M_n = 9300, M_w = 39 000, PDI = 4.19, 45% branching) and 48 h (97.3%, M_n = 16 300, M_w = 410 100, PDI = 25.2, 90% branching).

^{1}H NMR ($CDCl_3$, 298K, 400 MHz, ppm from TMS): 3.51-(s(or t), O−CH_3 of MMA), 3.70(s, O−CH_3 of EGDMA), 4.05(s, −O−CH_2−CH_2−O− of cross-linked EGDMA), 4.20,4.35(s, −O−CH_2−CH_2−O− of pendant EGDMA), 6.20(s, =CH_2 of pendant EGDMA), 7.44(t, p−CH of 2-(2-cyanopropyl) dithiobenzoate).

Chain Extension Polymerizations Using Hyperbranched PMMA as MacroCTA. Two hyperbranched PMMAs that were obtained via RAFT polymerization were used as macro chain-transfer agents (macroCTAs) to mediate the polymerization of styrene. The hyperbranched PMMA was first precipitated in hexane. The molecular weights, polydispersity (PDI), and molecular chain structures were determined by SEC and by ^{1}H NMR, respectively (see Table 2). The molecular chain structure of the two precursors indicated that nearly 100% of EGDMA had reacted. A typical polymerization with hyperbranched PMMA of M_n = 8970 g/mol and PDI = 4.61 used a ratio of macroCTA/styrene/AIBN was set to 1:500:0.1. MacroCTA (0.359 g, 0.04 mmol), styrene (2.00 g, 0.02 mol), and AIBN (0.316 g, 0.20 mol) were dissolved in 8.00 g of

Table 2. Structural Parameters of Hyperbranched Poly(methyl methacrylate) (PMMA) Precursors Synthesized From Series F1 (P_{F1}) and F2 (P_{F2}) Used for the Reversible Addition Fragmentation Chain Transfer Polymerization of Styrene[a]

	molar ratios						
precursor	CTA	MMA	EGDMA	$EGDMA_C$	M_n (g/mol)	M_w (g/mol)	PDI
P_{F1}	1	20	0.02	1.16	8970	41 300	4.61
P_{F2}	1	34	0.08	1.82	17 800	686 400	38.63

[a] Molar ratios of chain-transfer agent (CTA), methyl methacrylate (MMA), ethylene glycol dimethacrylate monoreacted (EGDMA) and direacted ($EGDMA_c$), azobis(isobutyronitrile) (AIBN), and molecular weight (M_n, M_w) and polydispersity (PDI) determined via size exclusion chromatography calibrated with linear PMMA as standards (molecular weight range: 1 944 000−1020 g/mol).

toluene. The polymerizations were left for 48 h, following the procedure described above. After polymerization, products were precipitated in hexane and analyzed by SEC and DSC. Conversion = 70%; M_n = 20 900 g/mol; PDI = 21.5.

Results and Discussions

Synthesis of Hyperbranched PMMA via RAFT Polymerization and Structure Characterization of the Resulting Polymeric Products. Chong et al. have studied the effect of the R group in a chain-transfer agent for RAFT polymerization.[23] They showed that compounds with R = $-C(Me)_2Ph$ or $-C(Me)_2CN$ control the living polymerization of methacrylate monomers, with polydispersities as low as 1.1. CPDB was therefore chosen as the chain-transfer agent to mediate the RAFT copolymerization of MMA and EGDMA.

The hyperbranched PMMAs were prepared as described in the Experimental Section, using two feed ratios (see Table 1), following the work of Sherrington and co-workers.[12−14] In their initial work, the authors synthesized branched PMMAs, via a one-pot solution free-radical polymerization, in the presence of a conventional chain-transfer agent (dodecanethiol, DDT), to inhibit gelation.[12] Their study showed that when the ratio of EGDMA/DDT is higher than 1.5, gelation occurs in the polymerization system. In a more recent communication, Sherrington's and Armes' groups report the use of living polymerization techniques (ATRP and GTP, respectively) to produce hyperbranched PMMA,[13] and they reported a feed ratio of MMA/EGDMA/initiator of 100:5.86:5.04 as the highest EGDMA:initiator ratio achievable without risk of gelation. In RAFT polymerization, the chain-transfer agent also acts as a living polymerization initiator for the polymeric chains. We therefore studied the effect of the ratio CPDB/EGDMA for developing hyperbranched polymers, and compare the effect of CPDB to that of a traditional chain-transfer agents (from Sherrington's initial study) and to that of a living polymerization initiators. We used a ratio of EGDMA/CTA (5.85:5.04) ~1 (series labeled F1) and a ratio (5.85:3.0) ~2 (series labeled F2) in order to compare our results with previously published work. AIBN, commonly introduced in the RAFT process to generate radicals that subsequently trigger the chain transfer process, was used at one tenth of the amount of CTA to minimize free-radical termination reactions.

The monomer conversions were determined by ^1H NMR spectroscopy following eq 1, where I_{CH_2} is the integral value of the peak at 6.2 ppm corresponding to one proton of the double bond ($=CH_2$) of unreacted MMA and I_{OCH_3} is the integral value of the signal at 3.5−3.9 ppm [$O-CH_3$ of both reacted (i.e., incorporated in a PMMA chain) and unreacted MMA].

$$\text{Conversion}(\%) = \frac{I_{OCH_3} - 3 \times I_{CH_2}}{I_{OCH_3}} \times 100 \quad (\text{Eq.1})$$

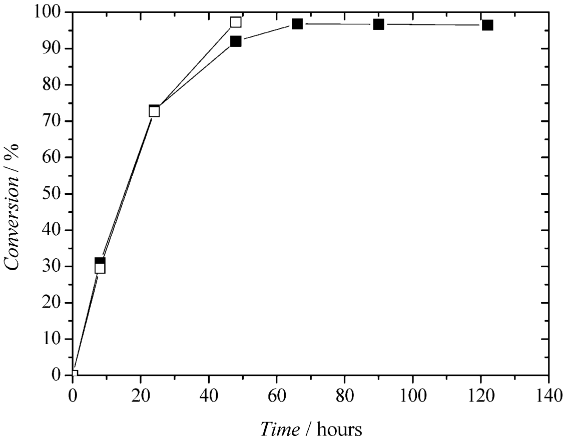

Figure 1. Monomer conversion for series F1 (■, CTA/MMA/EGDMA/AIBN = 5.04:100:5.85:0.50) and F2 (□, CTA/MMA/EGDMA/AIBN = 3.00:100:5.85:0.30)) during the reversible addition fragmentation chain-transfer copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethyl methacrylate (EGDMA) mediated by 2-2′-cyanopropyl dithiobenzoate (CPDB = CTA) at 60 °C in toluene, initiated by azobis(isobutyronitrile) (AIBN).

Figure 1 shows the monomer conversion with time for the series F1 and F2. Both series of reactions reached high conversions (~97%), and there was little difference between series F1 and F2 under these reaction conditions. This is a surprising result, as it is usual to observe a retardation effect on the polymerization when the concentration of CTA is increased. As no clear explanations are available at the present time, further experiments are currently being undertaken to elucidate the effect of the branching agent on the kinetics of polymerization. The difference in CTA/EGDMA ratios led to different polymeric architectures. Indeed, while the series F1 (EGDMA/CTA ≈ 1) led to the production of hyperbranched polymers up to 97% conversions, the occurrence of gelations at high conversions were observed for the F2 series (EGDMA/CTA ≈ 2).

^1H and ^{13}C NMR spectroscopy have been previously used to determine the structure of branched copolymers of MMA and EGDMA.[5,12,24] In this work, the presence of a benzoate moiety at the polymeric chain ends brings further information on the ratio CTA/EGDMA for each hyperbranched polymer molecule. A typical ^1H NMR spectrum of hyperbranched PMMA is shown in Figure 2. From the ratio of the integrated intensities at 7.4 ppm (calibrated as 1.00) and at 6.00 ppm, one can determine the molar ratio of pendant EGDMA incorporated in the molecular chain; the integrated intensity from 4.3 to 3.95 ppm can be used to calculate the amount of EGDMA bridging the PMMA chains. Also, the ratio of MMA can be deduced by using the integration at 3.10−3.70 ppm. The molar ratios of the components for each of the hyperbranched polymers are summarized in Table 3 for Series F1 and Series F2.

Table 3. Molar Ratios Determined by ^{1}H NMR of Chain-Transfer Agent (CTA), Methyl Methacrylate (MMA), Ethylene Glycol Dimethacrylate Monoreacted (EGDMA), and Direacted (EGDMA$_c$) to Determine the Backbone Architectures of Series F1 and Series F2

series F1		series F2	
conv. (%)	CTA/MMA/EGDMA/EGDMA$_c$	conv. (%)	CTA/MMA/EGDMA/EGDMA$_c$
31.0	1.00:12.0:0.67:0.43	29.5	1.00:13.0:1.08:0.46
73.0	1.00:17.0:0.10:1.06	72.7	1.00:20.0:0.87:0.98
92.0	1.00:25.0:0.06:1.10	97.0	1.00:27.0:0.21:1.74
96.8	1.00:23.0:0.00:1.18	97.4	partial gelation
96.7	1.00:25 0:0.00:1.26	98.1	gelation
96.5	1.00:23.0:0.00:1.13	99.6	gelation

Table 4. Molecular Weights and Polydispersities (PDI) of Series F1 and Series F2 during Methyl Methacrylate Polymerization Determined via Size Exclusion Chromatography Calibrated with Linear PMMA as Standards (Molecular Weight Range: 1 944 000−1020 g/mol)

series F1				series F2			
conv. (%)	M_n(g/mol)	M_w(g/mol)	PDI	conv. (%)	M_n(g/mol)	M_w(g/mol)	PDI
31.0	2800	3700	1.32	29.5	2800	4200	1.52
73.0	6100	18 700	3.04	72.7	9300	39 000	4.19
92.0	9700	47 600	4.89	97.0	16 300	410 100	25.2
96.8	8600	48 800	5.48	97.4	partial gelation		
96.7	9100	41 700	5.18	98.1	gelation		
96.5	9100	45 700	5.06	99.6	gelation		

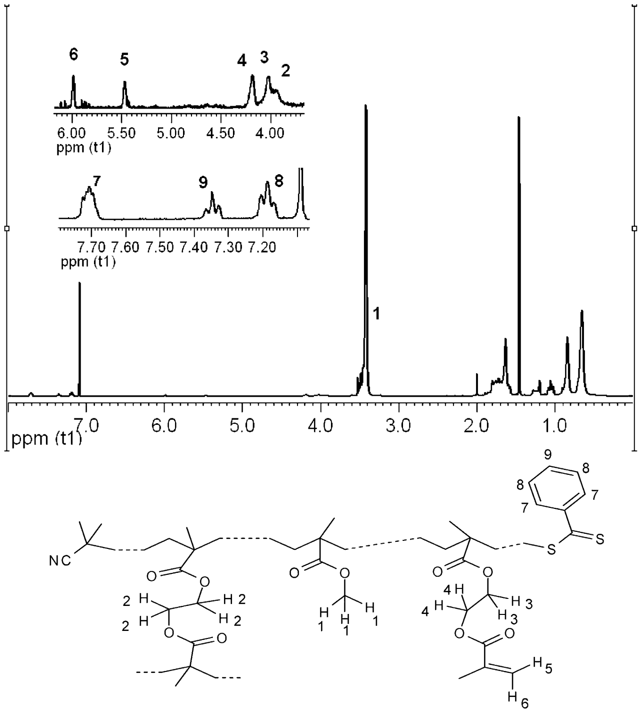

Figure 2. ^{1}H NMR spectrum for a typical poly(MMA-*co*-EGDMA) (Series F1, 31% conversion) synthesized via reversible addition fragmentation chain transfer polymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), and after precipitation in hexane.

From Table 3, it is obvious that during polymerization the ratio of cross-linked EGDMA (EGDMA$_c$) increases while the ratio of pendant EGDMA decreases. Furthermore, the total amount of EGDMA in the reaction system is constant during reaction, with EGDMA + EGDMA$_c$ = 1.16 for Series F1 (CTA/EGDMA = 5.04:5.85 = 1:1.16) and 1.95 for Series F2 (CTA/EGDMA = 3.0:5.85 = 1:1.95), respectively. Slight discrepancies are attributed to experimental errors arising form the integration of the ^{1}H NMR spectra. The experimental results also showed that EGDMA seems to be incorporated in the polymeric chains faster than MMA. This is an effect of statistics, as EGDMA has two reactive groups and is thus twice as likely to be incorporated than MMA. In theory, a maximum of 20 MMA units was expected to be incorporated in the polymeric chain in Series F1 (CTA/MMA = 5.04:100 = 1:20) and 33.3 units in Series F2 (CTA/MMA = 3.0:100 = 1:33.3). The experimental data fit well with theory, within reasonable experimental error, due to ^{1}H NMR spectra integration at high monomer conversion.

Table 4 shows the changes in molecular weight and polydispersity for the Series F1 and Series F2 during polymerization. For both Series F1 and F2, the molecular weight increases regularly with conversion. In the case of Series F1, the change in molar mass slows down after 96.8% conversion (48 h). The polydispersity also increases rapidly and levels off after similar conversion levels have been achieved. Comparison of the two series demonstrates that the molecular weights and PDIs of Series F2 are higher than those of Series F1, at similar reaction times. This can be accounted for by the higher molar ratio of EGDMA to CTA in Series F2. This leads to a higher bifunctional vinyl group concentration in the samples identified in Series F2, resulting in a weaker control on the polymer structure. By comparing Series F1 to the copper-mediated LRP conducted by Sherrington and Armes with similar molar ratios, it is observed that RAFT polymerization leads to better control over the molecular weight and molecular weight distribution. Indeed, the maximum PDI obtained by RAFT is 5.5, while copper-mediated LRP leads to a PDI of 63.3 under similar conditions.[13] Furthermore, conventional free-radical polymerization led to gelation for molar ratios of EGDMA to CTA that are higher than 1.5. In RAFT polymerization, gelation occurs at a molar ratio that is near to 2 (series F2), at high conversion (>97%), with the PDI reaching only 25.0 before gelation.

The molecular weights that were determined in our study are not as high as those expected for a classic living polymerization system. Indeed, the data obtained from SEC, using a differential refractive index (DRI) as detector, are usually lower than the real molecular weight, as branched polymers of a given molecular weight have a smaller hydrodynamic volume than is possessed by a linear polymeric chain of similar molecular weight.

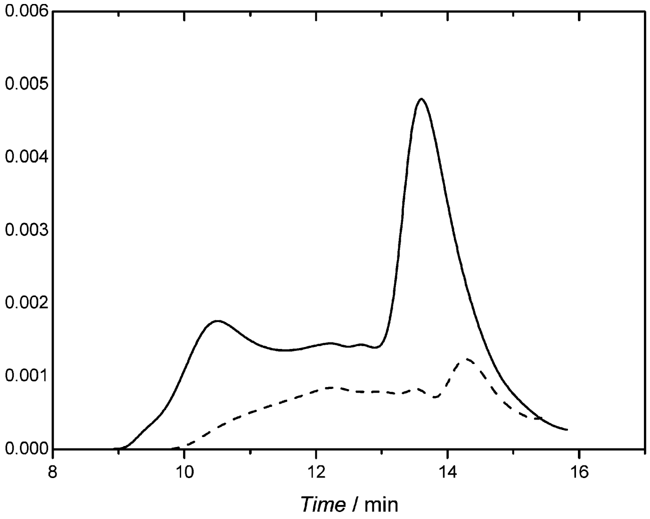

Figure 3. Evolution of molecular weight distribution as measured by UV detection at 256 nm before (- -) and after chain extension of hyperbranched polymethyl methacrylate (PMMA, $M_n = 8{,}970$ g/mol, $PDI = 4.61$, branching ≈ 100%) with styrene (−). The response of the signal before chain extension (y axis) has been multiplied by 3 in order to enhance the clarity of the figure.

Chain Extension of the Hyperbranched Polymers—Synthesis of Multi-Arm Star Polymers. RAFT polymerization is a great tool for the straightforward, one-pot, synthesis of hyperbranched polymers by controlling the polymerization of a monofunctional monomer and by controlling the incorporation of a difunctional monomer along the backbone. Moreover, RAFT polymerization is a living process, which means that all chains should exhibit a reactive dithioester end group at the end of the polymerization (if the polymeric chains formed from the initial free-radical initiator are neglected). Therefore, addition of a new batch of monofunctional monomer should lead to the chain extension of the hyperbranched polymer and result in a starlike structure, with the hyperbranched polymer acting as the core and the linear extended chains as the arms. This would offer a similar structure as that synthesized by Davis and co-workers, using a polyester dendrimer as core and growing polystyrene arms via RAFT, but offers a more versatile synthetic route to the hyperbranched core.[25] We therefore designed a series of experiments in order to test the reactivity of the hyperbranched polymer end groups. Two hyperbranched PMMAs obtained via RAFT polymerization (following ratios from Series F1 and F2) were used as macroCTAs to mediate the polymerization of styrene (see Experimental Section and Table 3). Both macroCTA precursors were chosen with EGDMA reacted at near 100%, and the polymerizations were carried out using a ratio of macroCTA/styrene/AIBN = 1:500:0.1. Products were analyzed by SEC and DSC. In both cases, SEC analyses show a clear increase of molecular weight distributions toward high molecular weights (Figure 3). As the polydispersities of the starting material are very high, the highest values of molecular weight are already reaching the limit of exclusion of our SEC system, but the low-molecular-weight values are remarkably shifted toward higher values, confirming the insertion of new polymeric chains. To further verify the presence of polystyrene chains, we used dual DRI/UV detection on our SEC system, setting the absorption wavelength to 256 nm (corresponding to the aromatic ring of the styrene).

Table 5. Glass Transition Temperatures for Hyperbranched Poly(methyl methacrylate) (PMMA) Obtained from Series F1 (CTA/MMA/EGDMA/AIBN = 5.04:100:5.85:0.50) and Series F2 (CTA/MMA/EGDMA/AIBN = 3.00:100:5.85:0.30), Star Copolymers Polystyrene (PS)−Hyperbranched PMMA Synthesized Using Precursor from Series F1 (S_{F1}) and Series F2 (S_{F2}), Linear PMMA, Linear PS, and PS Synthesized via the Reversible Addition Fragmentation Process (PS_{RAFT})

samples	conv. (%)	$T_{g,1}$(°C)	$T_{g,2}$(°C)
series F1	31.0		77.2
	73.0		101.7
	92.0		105.1
	96.8		107.3
series F2	29.5		76.3
	72.7		134.0
	97.0		139.0
	97.4		137.9
S_{F1}		95.9	112.9
S_{F2}		110.1	129.9
PMMA		122.3	
PS_{RAFT}		80.0	
PS		100.0	

Figure 3 shows the weak signal of the PMMA-based macroCTA (still observable due to the weak absorption at this wavelength of the dithioester end groups) and the strong signal of the polymer after styrene polymerization, confirming the insertion of the polystyrene chains (in Figure 3, the signal intensity of PMMA has been multiplied by a factor of 3 to show more clearly the PMMA macroCTA).

Thermal Analyses of Branched PMMA Produced via RAFT Polymerization. A number of reports have considered the effect of molecular weight on the T_g of polymers.[26,27] Hyperbranched polymers usually have lower T_g values than their linear counterparts.[28,29] Some reports on the T_g of highly branched polymers indicated that the T_g values are greatly affected by terminal functional groups,[30,31] with decreases in T_g following increases in the concentration of chain end groups.[32] Furthermore, the restriction in mobility that is caused by the branching points should increase T_g. DSC analyses were performed on samples from Series F1 and F2 that were obtained after various polymerization times (Table 5). As expected, the hyperbranched poly(MMA-*co*-EGDMA) samples from Series F1 show lower T_g's than those of linear PMMA ($T_g = 105$ °C as an average for the hyperbranched polymer and $T_g = 122.3$ °C, for a linear PMMA, Tables 5). Furthermore, T_g increases with reaction time up to a maximum value, due to the further reaction of pendant double bonds from the backbone, to generate further branching.[25]

In the case of samples from Series F2, cross-linking reduced the chain's flexibility and eventually increased the T_g (135 °C as an average). EGDMA acts as both branching agent and cross-linker, and with the polymerization process proceeding, more pendant groups from EGDMA are incorporated in the backbone of polymers and generate bridges between chains, thus increasing T_g, as the molecular chain length between branches becomes smaller than that required for cooperative segmental motion.

Hyperbranched-core star polymers have great potential for a variety of applications, as it is possible to design high-molecular-weight star polymers with tunable arm lengths and core sizes. In addition to the obvious rheological properties of these architectures, they can also be used as compatibilizers. Indeed, analyses by DSC show that the star copolymer has two

T_g's. The lowest T_g corresponds to the polystyrene chains ($T_{g,1}$ (S_{F1}) = 95.9 °C and $T_{g,1}$ (S_{F2}) = 110.1 °C, while for a linear polystyrene chain, T_g (PS) $\approx$ 100 °C (a polystyrene chain produced by RAFT polymerization, using a similar ratio of CTA/styrene as for the macroCTA-mediated polymerization, was analyzed by DSC, and a T_g of 80 °C was obtained). The highest T_g ($T_{g,2}$ (S_{F1}) = 112.9 °C and $T_{g,2}$ (S_{F2}) = 129.9 °C) agrees well with the values measured for the hyperbranched PMMA precursors. Therefore, these analyses not only confirm the incorporation of polystyrene chains on the hyperbranched PMMA but also show that phase separation occurs in a similar manner to what is usually observed for block copolymers of PMMA-*b*-PS.[33,34] It is therefore possible to use the hyperbranched PMMA core as a polar environment to encapsulate 'polar' moieties before mixing the 'star' architecture in a nonpolar, hydrophobic matrix with the styrene arms acting as compatibilizers. Testing to assess the compatibilizing properties of such compounds is currently being undertaken in our laboratories.

Conclusion

The RAFT-mediated polymerization was applied for the first time to prepare hyperbranched PMMA with EGDMA as the branching agent. A soluble, branched, PMMA with near 100% monomer conversion was obtained. The effects of the molar ratio of chain-transfer agent/cross-linker, temperature, and polymerization time have been investigated. The chain architecture was estimated by NMR analyses. The branching and cross-linking process of the MMA−EGDMA system is well controlled by the use of RAFT polymerization. The branched PMMAs obtained via RAFT-agent-mediated polymerization presented a narrow polydispersity and lower T_g and were able to initiate further polymerization when a new batch of monomer was added.

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