Macromolecules

Synthesis, Characterization and Thermolysis of Hyperbranched Homo- and Amphiphilic Co-Polymers Prepared Using an Inimer Bearing a Thermolyzable Acylal Group

Maria Rikkou-Kalourkoti,[†] Krzysztof Matyjaszewski,[‡] and Costas S. Patrickios^{†,*}

[†]Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus [‡]Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States



ABSTRACT: Degradable hyperbranched polymers were synthesized via self-condensing atom transfer radical copolymerization of methyl methacrylate (MMA) with a novel inimer bearing a thermolyzable acylal group. This inimer was 1-(2bromoisobutyryloxyl)ethyl methacrylate (BIB1EMA) and was synthesized in a one-step reaction between 2-bromoisobutyric acid and vinyl methacrylate at 40% yield. The inimer was subsequently used for the preparation of three degradable hyperbranched homopolymers of MMA (monomer conversion ~80%) with molecular weights in the range from 36 000 to 51 000 g mol⁻¹ synthesized using initial MMA-to-inimer molar ratios between 25 and 100. The inimer was also used for the preparation of two degradable hyperbranched amphiphilic copolymers of MMA and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with an MMA hydrophobic hyperbranched core and different compositions, 10 and 38 mol % DMAEMA, afforded by changing the relative loadings in the two comonomers. Both hyperbranched amphiphilic copolymers were soluble in THF: water mixtures with up to 50% w/w water content, whereas they precipitated at higher water contents. All hyperbranched (co)polymers were thermolyzed in a vacuum oven at 200 °C within 24–56 h. The molecular weights of the thermolysis products were consistent with the inimer content and the complete thermolysis of the hyperbranched (co)polymers. Hyperbranched polymers of MMA, also prepared in this investigation, but using a nondegradable inimer, isomeric to BIB1EMA, 2-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB2EMA), did not present any reduction in their molecular weight when subjected to the same thermolysis conditions as those applied for the degradable hyperbranched polymers (200 °C, ~24 h).

INTRODUCTION

Hyperbranched polymers represent an interesting macromolecular architecture, with features intermediate between those of linear polymers and polymer networks. Similar to polymer networks, hyperbranched polymers are highly branched, but yet soluble as linear polymers. As mentioned in the review by Hult et al.,1 hyperbranched polymers were first reported by DuPont in an effort to replace dendrimers, also highly branched polymers but of highly ordered structure which are difficult and time-consuming to prepare and, therefore, less appropriate for industrial use. The high degree of branching of hyperbranched polymers is responsible for their unique physical properties, such as their compact shape resulting in low viscosity in solution and in the molten state compared to their linear counterparts,^{2,3} and their large number of functional groups on their periphery. Because of these properties, hyperbranched polymers^{4–6} find numerous applications in surface modification,^{7–12} in coatings,^{13–16} in controlled drug and gene delivery,^{17,18} in nonlinear optics,^{19,20} and can form the cross-linking nodes in designer's hydrogels.^{21–25} As mentioned before, the main advantage of hyperbranched polymers compared to dendrimers is their facile synthesis.

Hyperbranched vinyl polymers can be synthesized following three different techniques: (a) copolymerization of monovinyl

with small amounts of di- or multivinyl monomers, (b) polymerization of di- or multivinyl monomers with a large excess of initiator, and (c) self-condensing vinyl polymerization of AB* initiator-monomers, known as *inimers*. Whereas the first two techniques can be applied using either controlled or conventional polymerization methods, the third technique requires the use of a controlled polymerization method. Of special interest are the different *controlled radical* polymerization methods which have been used for the preparation of hyperbranched polymers applying all three above-mentioned techniques, including atom transfer radical polymerization (ATRP),^{26–32} reversible addition–fragmentation chain transfer polymerization (RAFT),^{33–40} and nitroxide-mediated radical polymerization (NMP).^{41–44} Furthermore, controlled/"living" ionic polymerization methods have also been used for the synthesis of hyperbranched polymers, including "living" cationic polymerization⁴⁵ and group transfer polymerization (GTP).^{46–49}

In the present study, self-condensing vinyl copolymerization of a degradable inimer bearing a thermally labile acylal group

Received:September 5, 2011Revised:December 27, 2011Published:January 19, 2012

was performed via ATRP for the preparation of hyperbranched polymers. ATRP has previously been employed several times for the preparation of hyperbranched polymers using inimers,^{26-30,50} but only once did that involve degradable inimers.³¹ Those degradable inimers bore disulfide or ester labile groups and were used for the preparation of degradable hyperbranched hydrophobic homopolymers of styrene.³¹ In this report, we present the synthesis of thermally labile hyperbranched hydrophobic homopolymers and amphiphilic copolymers using a novel inimer bearing an acylal group. The successful thermolysis of these polymers and the results from the characterization of the thermolysis products are also presented. Finally, to show that the thermal cleavage of the present hyperbranched polymers was due to the thermolysis of the thermally labile inimer residue in the polymers, we also prepared similar hyperbranched polymers based on a nondegradable inimer, isomeric to the thermolyzable one. When subjected to the same thermolysis conditions as those used for the former (thermolyzable) polymers, these latter polymers did not present any reduction in their molecular weight.

EXPERIMENTAL SECTION

Materials and Methods. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, 99%) and methyl methacrylate (MMA, 99%) were purchased from Aldrich, Germany. Copper(I) bromide (99%), 2,2'-bipyridine (bpy, 99%), 2-bromoisobutyric acid (98%), vinyl methacrylate (98%) and 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%) were also purchased from Aldrich and were used as received. *N*,*N*-Dimethylformamide (DMF, Merck, 99%) was dried over calcium hydride and was freshly distilled under reduced pressure. The monomers were passed through basic alumina columns to remove the polymerization inhibitor and any other acidic impurities and they were stirred overnight over calcium hydride to remove the last traces of moisture and protonic impurities. This was done in the presence of an added free radical inhibitor, DPPH, to avoid undesired thermal polymerization. The monomers were freshly distilled prior to the polymerization.

Preparation of the Degradable Acylal Inimer 1-(2-Bromoisobutyryloxyl)ethyl Methacrylate (BIB1EMA). The degradable inimer BIB1EMA was prepared by an addition reaction. In particular, to a 100 mL round-bottomed flask containing 5 mL of vinyl methacrylate (4.67 g, 0.042 mol) were added 10.42 g of 2bromoisobutyric acid (0.062 mol) and left to react at 95 °C for 19 h until all vinyl methacrylate was consumed. As vinyl methacrylate already contained radical inhibitor, no extra inhibitor was added to this reaction. After 19 h, the mixture was allowed to cool down and was distilled under vacuum. The desired product was isolated at 40% yield as a yellowish liquid. The structure of the inimer was confirmed by ¹H and ¹³C NMR spectroscopy. ¹H NMR (300 MHz, CDCl₃, δ): 6.87 (*m*, 1×1 H, -OCHH(CH₃)O-), 6.09 (s, 1×1 H, CH₂=C-, H *cis* to the carboxylate), 5.57 (s, 1×1 H, CH₂=C-, H trans to the carboxylate), 1.87 (s, $2 \times 3H$, $-C(CH_3)_2Br$), 1.81 (s, $1 \times 3H$, $-C(CH_3)=CH_2$), 1.49 (d, $1 \times 3H$, $-OCHH(CH_3)O-$). ¹³C NMR (300 MHz, CDCl₃, δ): 169.6 (1C, (CH₃)₂BrC-COO-), 165.1 (1C, CH₂=C(CH₃)-COO-), 135.3 (1C, $CH_2=C(CH_3)-$), 127.0 (1C, $CH_2=C(CH_3)-$), 89.9 (2C, -OCH(CH₃)O-), 55.1 (1C, -C(CH₃)₂Br), 30.4 (2C, $-C(CH_3)_2Br)$, 19.1 (2C, $-OCHH(CH_3)O-$), 18.0 (1C, $-C(CH_3)=$ CH_{2}).

Preparation of the Nondegradable Inimer 2-(2-Bromoisobutyryloxyl)ethyl Methacrylate (BIB2EMA). The nondegradable inimer BIB2EMA was prepared by an esterification reaction. In particular, to a 100 mL round-bottomed flask containing 5 mL of 2-hydroxyethyl methacrylate (5.35 g, 0.041 mol) and 34 mL of triethylamine (24.9 g, 0.25 mol) was added 7.62 mL of 2bromoisobutyryl bromide (14.00 g, 0.062 mol). The reaction was carried out under a dry nitrogen atmosphere at 0 °C. The resulting insoluble salt of Et₃N-HBr was removed from the reaction mixture by filtration. Subsequently, the filtrate was passed through a column of basic alumina to remove the formed (excess) isobutyric acid. The desired product was finally obtained after vacuum distillation at 90 °C as a yellowish liquid at 43% yield. The structure of the inimer was confirmed by ¹H and ¹³C NMR spectroscopy. ¹H NMR (300 MHz, CDCl₃, δ): 6.06 (*s*, 1 × 1H, CH₂=C-, H *cis* to the carboxylate), 5.52 (*s*, 1 × 1H, CH₂=C-, H *trans* to the carboxylate), 4.35 (*s*, 2 × 2H, -OCHH₂CH₂O-), 1.87 (*s*, 2 × 3H, -C(CH₃)₂Br), 1.86 (*s*, 1 × 3H, -C(CH₃)=CH₂). ¹³C NMR (300 MHz, CDCl₃, δ): 171.4 (1C, (CH₃)₂BrC-COO-), 166.9 (1C, CH₂=C(CH₃)-COO-), 135.8 (1C, CH₂=C(CH₃)-), 126.1 (1C, CH₂=C(CH₃)-), 63.5 (1C, -OCH₂CH₂O-), 61.8 (1C, -OCHH₂CH₂O-), 55.3 (1C, -C(CH₃)₂Br), 18.2 (1C, -C(CH₃)=CH₂).

Synthesis of the Hyperbranched Homopolymers. Polymerizations of Methyl Methacrylate Using 1-(2-Bromoisobutyryloxyl)ethyl Methacrylate (BIB1EMA). For the preparation of the degradable hyperbranched homopolymers of MMA, the initial monomer-tocatalyst (CuBr) molar ratio, the initial monomer concentration and the amount of the inimer loaded were kept constant at values of 100, 5 M and 5.4×10^{-4} mol, respectively. The initial monomer-to-inimer molar ratio was varied from 25 to 100. A typical experimental procedure for the preparation of BIB1EMA-co-MMA25 was as follows. A 20 mg sample of CuBr (1.4×10^{-4} mol), 65.4 mg of bpy (4.2×10^{-4} mol), 1.44 mL of MMA (1.34 g, 0.013 mol) and 1 mL of DMF were added into a dry 25 mL Schlenk tube kept under a dry nitrogen atmosphere. The reaction mixture was degassed by two freeze-pump-thaw cycles and then 0.15 g of inimer (5.4 \times 10⁻⁴ mol), dissolved in 0.25 mL DMF, was added to the mixture. Subsequently, the Schlenk tube was placed in a thermostated oil bath at 70 °C for 2 h until monomer conversion reached 75%. The product of the polymerization reaction was passed through a short column of neutral alumina to remove copper, was precipitated in *n*-hexane and was finally dried in a vacuum oven at room temperature for 72 h.

Polymerizations of Methyl Methacrylate Using 2-(2-Bromoisobutyryloxyl)ethyl Methacrylate (BIB2EMA). For the preparation of the nondegradable hyperbranched homopolymers of MMA, a similar procedure was followed as that employed for the preparation of the degradable hyperbranched homopolymers described above, with the only difference that the nondegradable BIB2EMA inimer was used instead of BIB1EMA.

Synthesis of the Degradable Hyperbranched Amphiphilic Copolymers. For the preparation of the degradable hyperbranched amphiphilic copolymers, copolymerizations by sequential addition of monomers were performed. A typical procedure for the preparation of BIB1EMA-co-MMA₅₀-grad-DMAEMA₅₀ is described below. To a 25 mL dry Schlenk tube kept under a dry nitrogen atmosphere were added 39.3 mg of CuBr (2.7×10^{-4} mol), 0.13 g of bpy (8.2×10^{-4} mol), 2.87 mL of MMA (2.69 g, 0.026 mol), and 2.0 mL of DMF. The mixture was degassed by two vacuum-nitrogen cycles. The reaction flask was heated to 70 °C and a deoxygenated solution of the BIB1EMA degradable inimer (0.15 g, 5.4×10^{-4} mol) in 0.5 mL of DMF was added. After 85 min of reaction, at a monomer conversion of 78%, samples were extracted for gel permeation chromatography (GPC) and ¹H NMR spectroscopy analyses (polymer relative numberaverage molecular weight, $M_n = 11\ 000\ \text{g mol}^{-1}$, polydispersity index, PDI = M_w/M_n = 2.34; M_w is the relative weight-average molecular weight). Then, the second monomer, DMAEMA (4.5 mL, 4.20 g, 0.027 mol) was added and was allowed to react for another 120 min until the DMAEMA conversion reached 54%. As with the hyperbranched MMA homopolymers, work-up procedure involved passage through neutral alumina, precipitation in *n*-hexane and vacuum drying at room temperature for 72 h.

Thermolysis of the Hyperbranched (Co)Polymers. All hyperbranched (co)polymers were subjected to thermolysis at 200 °C to cleave the acylal group in the inimer residues. Samples (\sim 0.5 g) of each hyperbranched polymer in glass vials were placed in a vacuum oven kept at 200 °C for about 24 h. Samples were taken out of the oven at different times during thermolysis and characterized using GPC to estimate the extent of thermolysis.

Macromolecules

Polymer Characterization. Gel Permeation Chromatography (GPC). The molecular weight distributions (MWDs) of all the hyperbranched (co)polymers and their thermolysis products were recorded using GPC with single detection based on refractive index (RI), from which the relative M_{n} , the relative M_w , and the PDIs were calculated. This setup will be referred to as the GPC–RI system. A single Polymer Laboratories PL-Mixed "D" column (bead size =5 μ m; pore sizes =100, 500, 10³ and 10⁴ Å) was used for sample analysis. The mobile phase was THF, delivered using a Waters 515 isocratic pump at a flow rate of 1 mL min⁻¹. The RI signal was measured using a Polymer Laboratories ERC-7515A RI detector. The calibration curve was based on eight narrow MW (630, 2680, 4250, 13000, 28900, 50000, 128000, and 260000 g mol⁻¹) linear polyMMA standards also supplied by Polymer Laboratories.

NMR Spectroscopy. A 300 MHz Avance Bruker spectrometer equipped with an Ultrashield magnet was used to acquire the ¹H NMR spectra of all the hyperbranched (co)polymers in CDCl₃ containing traces of CHCl₃ which was used as an internal reference. The same instrument was also used to collect the ¹H and ¹³C NMR spectra of the two inimers synthesized.

Static Light Scattering. The absolute $M_{\rm w}$ of the hyperbranched polymers was measured using dual RI and static light scattering (SLS) detection in a GPC configuration (GPC-SLS system). To this end, a Brookhaven molecular weight analyzer (BI-MwA) equipped with a 30 mW red diode laser emitting at 673 nm and a multiangle detector, was used to determine the intensity of the scattered light at 7 different angles, 35°, 50°, 75°, 90°, 105°, 130°, and 145°, whereas a PL-RI 800 RI detector was used to simultaneously measure the RI signal. A Polymer Laboratories PL-LC1120 isocratic pump was used to deliver the THF mobile phase at a flow rate of 1 mL min⁻¹ through a PL-Mixed "D" column, also supplied by Polymer Laboratories. The analysis for the calculation of the absolute M_w was conducted using the PSS-WinGPC 7 SLS-flow software. The hyperbranched (co)polymers were dissolved in HPLC-grade THF at a 2% w/v polymer concentration and were filtered through 0.45 μm pore size syringe filters. The RI increments (dn/dc) of the hyperbranched (co)polymer solutions in THF used for the calculation of the absolute M_w were 0.087 mL g^{-1} .

Dynamic Light Scattering (DLS). The hydrodynamic diameters of the synthesized amphiphilic hyperbranched copolymers in water/THF mixtures were measured using dynamic light scattering (DLS). A 1% w/w solution of each hyperbranched amphiphilic copolymer was prepared in the appropriate solvent mixture and was filtered three times through a PTFE syringe filter with 0.45 μ m pore size diameters. The filtered solution was left to settle for about an hour, so that any air bubbles could escape before the DLS measurement. A 90Plus Brookhaven DLS spectrophotometer, equipped with a BI9000 correlator and a 30 mW red diode laser emitting at 673 nm, was used to determine the intensity of the scattered light at a 90° angle. The data were processed using multimodal size distribution (MSD) analysis based on non-negatively constrained least-squares (NNCLS).

RESULTS AND DISCUSSION

Synthesis of the Degradable Inimer. For the preparation of the degradable hyperbranched (co)polymers via the selfcondensing vinyl copolymerization (SCVCP) technique and using ATRP, it was first necessary to design and synthesize the appropriate inimer. Thus, 1-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB1EMA) was synthesized. This molecule consists of one polymerizable methacrylate unit (colored blue in Figure 1) and one 2-bromoisobutyrate group (in green) capable of initiating the polymerization, interconnected by one thermolyzable acylal group (in red). As shown in Figure 1, the synthesis of the inimer was performed in a simple, one-stage addition reaction between vinyl methacrylate and 2-bromoisobutyric acid. The final inimer was isolated at 40% yield and was characterized using ¹H and ¹³C NMR spectroscopy. Its NMR spectra are also presented in Figure 1.



Figure 1. Reaction scheme followed for the synthesis of the degradable inimer BIB1EMA and its structure confirmation by ¹H and ¹³C NMR spectroscopy.

Synthesis of the Nondegradable Inimer. As a control, the well-known nondegradable ATRP inimer 2-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB2EMA) was also prepared at 43% yield following the published procedure.⁵¹ It is noteworthy that this nondegradable inimer is isomeric to the degradable one, differing only in the arrangement of the ethyl group interconnecting the monomer and the initiator parts of the molecule. The chemical structures and the names of the two inimers and the two monomers used in this investigation are presented in Figure 2.



Figure 2. Chemical structures and names of the main reagents used for the preparation of the degradable and the nondegradable hyperbranched polymers using self-condensing ATRP.

Synthesis and Characterization of the Hyperbranched (Co)polymers. Degradable Hyperbranched Homopolymers of MMA. Before proceeding to the synthesis of the desired degradable hyperbranched polymers, a systematic study was performed to examine how important parameters, such as the initial monomer-to-inimer molar ratio and the initial monomer-to-catalyst molar ratio, influence the polymerization of MMA using the novel inimer BIB1EMA prepared for the needs of the present study. First, the effect of the initial monomer-to-catalyst molar ratio, μ , was examined by varying it in the range from 2.5 to 100, and keeping constant the initial monomer-to-inimer molar ratio, γ , at the value of 10. The polymerizations were performed at a constant initial monomer concentration of 3 M in DMF at 70 °C, and allowing a polymerization time of 2 h. Figure 3 presents the influence of the initial monomer-to-catalyst molar ratio on the M_n and the PDI values of the produced hyperbranched polymers as determined by GPC-RI.

As was expected, ⁵² both the M_n and the PDI values decreased as the initial monomer-to-catalyst molar ratio increased from



Figure 3. Dependence of number-average molecular weights (M_ns) and polydispersity indices (PDIs) on the initial monomer-to-catalyst molar ratio at an initial monomer-to-inimer molar ratio of 10 and an initial monomer concentration 3 M in DMF at 70 °C.

2.5 to 100. A lower initial monomer-to-catalyst molar ratio corresponds to a higher catalyst concentration which leads to more extensive activation and more random initiation, resulting in the synthesis of polymers with greater branching. Higher catalyst concentrations also lead to higher polymerization rates, resulting in higher monomer conversions. These monomer conversions, as determined by ¹H NMR spectroscopy, along with the M_n and PDI values from GPC, are presented in Table 1.

The second parameter that was examined was the initial monomer-to-inimer molar ratio, γ . For this study, the polymerization conditions were the same as those described above ([MMA]₀ = 3 M in DMF at 70 °C) and the initial monomer-to-catalyst molar ratio, μ , was kept constant at μ = 50, while the initial monomer-to-inimer molar ratio was varied from 25 to 100. The M_n values of the three resulting hyperbranched MMA homopolymers are plotted against the initial monomer-to-inimer molar ratio as the open circles ([MMA]₀ = 3 M) in Figure 4. As shown in the figure, the M_n values increased with the initial monomer-to-inimer molar ratio, a behavior that has been described before.⁵² Unlike the M_n values, the PDIs and the monomer conversion in this case were not systematically affected by the initial monomer-to-inimer molar ratio (Table 1, entries 5–7).

As shown in Table 1, all the degradable hyperbranched polymers, synthesized at $[MMA]_0 = 3$ M, presented relatively low molecular weights. To produce hyperbranched polymers of



Figure 4. Dependence of the number-average molecular weights $(M_n s)$ on the initial monomer-to-inimer molar ratio at two different initial monomer concentrations, 3 and 5 M, in DMF at 70 °C, and at constant initial monomer-to-catalyst molar ratio of 50.

higher molecular weights, we decided to perform the rest of the syntheses at the higher initial MMA concentration of 5 rather than 3 M, at constant initial monomer-to-catalyst molar ratio equal to 50, and varied the initial monomer-to-inimer molar ratio from 25 to 100. The higher initial monomer concentration resulted in higher monomer conversion, around 80%, and also resulted in polymers with higher molecular weights, as shown in Figure 4 (closed triangles). The three degradable hyperbranched homopolymers of MMA prepared in this way were characterized in terms of their relative $M_{\rm n}$ s and PDIs using GPC–RI and also in terms of their absolute $M_{\rm w}$ using GPC–SLS, and the results are presented in Table 2.

As shown in Table 2 and in Figure 4 (closed triangles), an increase in the molecular weights was observed with an increase in the initial monomer-to-inimer molar ratio, as expected.⁴² The GPC–SLS absolute M_w -values, listed in Table 2, also increased with the initial monomer-to-inimer molar ratio but were higher than the GPC–RI relative molecular weights due to the compact nature of the hyperbranched polymers compared to the linear polyMMA GPC calibration standards. In fact, hyperbranched polymers prepared via SCVCP exhibit a high degree of branching, approaching 46.5% at full monomer conversion.⁵³

Nondegradable Hyperbranched Homopolymers of MMA. To compare the behavior of the novel degradable inimer with that of other inimers already reported in the literature, we performed the synthesis of nondegradable hyperbranched

Table 1. Number-Average Molecular Weights, Polydispersity Indices, Polymerization Conditions, and Monomer Conversions upon the Synthesis of the Hyperbranched Polymers Prepared from the Polymerization of MMA ($[MMA]_0 = 3 M$) Using BIB1EMA

					GPC-RI		
entry	polymer structure	γ^{a}	μ^b	conversion MMA (%)	M _n	$M_{ m p}$	$M_{\rm w}/M_{\rm n}$
1	BIB1EMA-co-MMA ₁₀	10	2.5	80	13 000	12 600	7.65
2	BIB1EMA-co-MMA ₁₀	10	25	76	9590	10 800	2.99
3	BIB1EMA-co-MMA ₁₀	10	50	63	4550	5910	1.91
4	BIB1EMA-co-MMA ₁₀	10	100	18	1380	1260	1.40
5	BIB1EMA-co-MMA ₂₅	25	50	31	2450	2860	1.47
6	BIB1EMA-co-MMA ₅₀	50	50	36	3660	3750	1.48
7	BIB1EMA-co-MMA ₁₀₀	100	50	48	10 900	12 600	2.06

" γ : initial monomer-to-inimer molar ratio; $\gamma = [MMA]_0 / [BIB1EMA]_0$. ^b μ : initial monomer-to-catalyst molar ratio; $\mu = ([MMA]_0 + [BIB1EMA]_0) / [CuBr]_0$.

Table 2. Number-Average Molecular Weights, Absolute Weight-Average Molecular Weights, Polydispersity Indices, Monomer Conversions, and Copolymer Compositions of the Hyperbranched (Co)polymers Synthesized at an Initial Monomer (MMA) Concentration of 5 M

		GPC-RI		GPC-SLS		conversion (%)			
entry	polymer structure	$M_{\rm n}$	$M_{\rm w}/M_{\rm n}$	M _{n(RI)}	$M_{ m w(LS)}$	$M_{\rm w}/M_{\rm n}$	MMA	DMAEMA	¹ H NMR % mol MMA
Degradable Hyperbranched Homopolymers									
1	BIB1EMA-co-MMA ₂₅	9600	1.71	6740	36 470	1.67	75	-	100
2	BIB1EMA-co-MMA ₅₀	11 700	1.88	14 970	44 300	1.80	82	-	100
3	BIB1EMA-co-MMA ₁₀₀	27 360	2.08	27 930	51 450	1.89	79	-	100
Degradable Hyperbranched Amphiphilic Copolymers									
4	BIB1EMA-co-MMA ₅₀	11 000	2.34	-	-	-	78	-	100
5	(BIB1EMA-co-MMA ₅₀)-grad-DMAEMA ₅₀	16 200	1.86	19 343	40 000	1.74	89	54	62
6	BIB1EMA-co-MMA ₁₀₀	16 700	2.51	-	-	-	77	-	100
7	(BIB1EMA-co-MMA ₁₀₀)-grad-DMAEMA ₅₀	26 900	2.48	25 100	57 200	2.08	80	50	90
Nondegradable Hyperbranched Homopolymers									
8	BIB2EMA-co-MMA ₂₅	9450	2.25	11 700	25 480	2.32	71	-	100
9	BIB2EMA-co-MMA ₅₀	15 700	2.67	26 540	67 670	2.17	76	-	100
10	BIB2EMA-co-MMA ₁₀₀	20 900	2.54	29 720	71 970	1.90	77	-	100

homopolymers of MMA at exactly the same conditions as the degradable one. For this purpose, we chose to prepare the inimer 2-(2-bromoisobutyryloxyl)ethyl methacrylate (BIB2E-MA) which is an isomer of the degradable inimer and has already been reported in the literature.⁵¹ Three hyperbranched MMA homopolymers were synthesized using this nondegradable inimer BIB2EMA at a constant initial monomerto-catalyst molar ratio equal to 50 and an initial monomer concentration equal to 5 M, and varied the initial monomer-toinimer molar ratio from 25 to 100. The nondegradable hyperbranched polymers were also characterized in terms of their relative M_ns and PDIs using GPC-RI and in terms of their absolute M_{ws} using GPC-SLS, and the results are presented in Table 2 too, together with those for the degradable ones. As shown in the table, the polymers prepared using BIB2EMA followed the expected trends⁵² and displayed similar relative $M_{\rm p}$ and PDI values to those of the degradable ones prepared using BIB1EMA.

Degradable Hyperbranched Amphiphilic MMA-DMAEMA Copolymers. The preparation of the degradable hyperbranched amphiphilic copolymers was performed in a two-step synthetic procedure, via sequential addition of monomers. In the first step, the degradable hydrophobic hyperbranched core was synthesized by the polymerization of MMA using BIB1EMA at the same conditions as those used for the synthesis of the hyperbranched MMA homopolymers described above ($\mu = 50$, $[MMA]_0 = 5$ M, DMF, 70 °C). After allowing MMA to polymerize up to \sim 80% conversion, the DMAEMA hydrophilic monomer was added to the polymerization reactor (without isolating the hyperbranched MMA homopolymer and removing the unreacted MMA monomer to enhance the "livingness" of the system), resulting in the formation of the degradable hyperbranched amphiphilic copolymers with a plausible gradient composition in the second segment (although not yet reported, the reactivity ratios for the DMAEMA-MMA pair under ATRP conditions should not be exactly equal to one). Thus, two degradable hyperbranched amphiphilic copolymers were prepared, in which the length of the hydrophilic blocks was kept constant (by using the same initial DMAEMA-toinimer molar ratio) but the size of the hydrophobic core was varied by using different initial MMA-to-inimer molar ratios. The degradable hyperbranched amphiphilic copolymers were also characterized in terms of their relative $M_{\rm n}$ s and PDIs, using

GPC-RI, in terms of their absolute M_w s using GPC-SLS and in terms of their compositions using ¹H NMR spectroscopy, and the results are also presented in Table 2.

Figure 5 presents the GPC-RI traces of the two degradable hyperbranched amphiphilic gradient copolymers as well as



Figure 5. GPC traces of the degradable hyperbranched amphiphilic gradient copolymers, traces 2, (BIB1EMA-*co*-MMA₅₀)-*grad*-DMAE-MA₅₀, and 4, (BIB1EMA-*co*-MMA₁₀₀)-*grad*-DMAEMA₅₀, along those of their hyperbranched homopolymer precursors, traces 1, BIB1EMA-*co*-MMA₅₀, and 3, BIB1EMA-*co*-MMA₁₀₀.

those of their hyperbranched MMA homopolymer precursors. The figure shows that the GPC traces of the copolymers were shifted to smaller elution volumes compared to the traces of the homopolymer precursors, indicating their successful synthesis. As shown in Table 2, the absolute M_{ws} of the hyperbranched amphiphilic copolymers determined using GPC-SLS were higher than the relative M_{ns} determined using GPC-RI for the same reasons explained before. The compositions of the hyperbranched amphiphilic copolymers were determined from the ¹H NMR spectra by ratioing the signal from the three methoxy protons (3.56 ppm) of the side group of the MMA units to the six protons in the two azamethyl groups (2.3 ppm) in DMAEMA. The thus-determined percentage of the hydrophobic units was found to be very close to that calculated on the basis of the comonomer feed ratio and monomer conversion.

Hydrodynamic Size of the Hyperbranched Amphiphilic Copolymers. Because of the amphiphilicity of the hyperbranched copolymers, their behavior in selective solvents was investigated. In particular, DLS was employed to determine the hydrodynamic diameters of the present hyperbranched amphiphilic copolymers in THF: water mixtures as a function of the solvent composition. It was expected that larger entities would form when the percentage of the selective solvent in the solvent mixture would increase, 54 provided that the copolymer was still soluble. Thus, before proceeding to the DLS measurements, the solubility of the hyperbranched amphiphilic copolymers in solvent mixtures with water contents from 0 to 100% w/w was evaluated. It was determined that the hyperbranched amphiphilic copolymer (BIB1EMA-co-MMA₅₀)-grad-DMAEMA₅₀ was completely soluble in solvent mixtures with up to 60% w/w water, while it precipitated at higher water contents. It was also found that the hyperbranched amphiphilic copolymer with higher MMA hydrophobic content, (BIB1EMA-co-MMA100)-grad-DMAEMA50, was soluble in solvent mixtures with only up to 50% w/w water, and precipitated in mixtures richer in water.

Table 3. Hydrodynamic Diameters of the Hyperbranched Amphiphilic Copolymers in THF: Water Mixtures of Different Solvent Compositions

polymer in 1% w/w concentration	water content (% w/w) in solvent mixture	hydrodynamic diameter (nm)
(BIB1EMA-co-MMA ₅₀)- grad-DMAEMA ₅₀	40	31.6
	50	31.5
	60	39.4
(BIB1EMA-co-MMA ₁₀₀)- grad-DMAEMA ₅₀	30	27.3
	40	32.7
	50	63.0

After establishing the water-solubility of the hyperbranched amphiphilic copolymers, DLS measurements were performed for solutions with water content lower than that corresponding to the solubility limit to determine the copolymer hydrodynamic diameters. The thus-determined hydrodynamic diameters are listed in Table 3. As shown in the table, an increase in the water content led to an increase in the hydrodynamic diameters of the formed entities. Although highly branched systems like the present one do not form micelles, the observed increase in the hydrodynamic size indicates some form of weak association between these amphiphilic copolymers.

Thermolysis of the Degradable Hyperbranched (Co)-Polymers. After their characterization, all the hyperbranched (co)polymers were thermolyzed in a vacuum oven at 200 $^{\circ}C^{55,56}$ for about 24 h. First, a kinetic study of the thermolysis of hyperbranched polymer BIB1EMA-co-MMA25 was performed by temporally following its thermolysis process by GPC. Figure 6a presents the GPC-RI traces of the thermolysis products at different times, whereas Figure 6b displays the temporal evolution of the relative $M_{\rm n}$ s and PDIs of the products produced during thermolysis. As shown in Figure 6, the molecular weights of the thermolysis products were gradually reduced, and the thermolysis of the hyperbranched polymer BIB1EMA-co-MMA₂₅ was completed within 24 h. It is noteworthy that thermolysis not only confers reduction in the molecular weight but also in the PDI, due to the ultimate formation of rather homogeneous linear polymer products with monomodal MWDs.

After the thermolysis kinetic study, all hyperbranched (co)polymers were thermolyzed, and the thermolysis products were characterized in terms of their relative M_n and PDI values using GPC–RI. These results are listed in Table 4. Complete thermolysis was evidenced by reduction in M_n and PDI, arising from the formation of linear and homogeneous polymer products with a monomodal MWD. The time required for the complete thermolysis of the larger hyperbranched polymers was longer than 24 h, reaching 32 and 56 h for the hyperbranched polymers BIB1EMA-*co*-MMA₅₀ and BIB1EMA-*co*-MMA₁₀₀. Table 4 also presents the theoretically expected molecular weights of the thermolysis products, calculated as (mass of monomer fed) × (monomer conversion)/(moles of inimer fed).

Finally, it is noteworthy that control experiments were performed by attempting the thermolysis of the three nondegradable hyperbranched polymers by subjecting them to the same cleavage conditions as those applied for the degradable ones. Molecular weight characterization using GPC-RI revealed that the relative M_n and PDI values of the processed polymers barely changed, indicating that no



Figure 6. (a) GPC traces of the samples taken during the thermolysis of the degradable hyperberanched MMA homopolymer BIB1EMA-co-MMA₂₅. (b) Temporal evolution of the relative M_n and PDI values during thermolysis.

Table 4. Molecular Weight Characteristics of the Products Formed upon Subjecting the Degradable and the Non-Degradable Hyperbranched (Co)polymers to Thermolysis Conditions (200 °C for ~24 h)

	be: thern	fore nolysis	thermolysis product			
hyperbranched polymer	M _n	$M_{\rm w}/M_{\rm n}$	$\mathrm{MW}_{\mathrm{theor.}}$	$M_{\rm n}$	$M_{\rm w}/M_{\rm n}$	
BIB1EMA-co-MMA ₂₅	9600	1.71	2230	2710	1.30	
BIB1EMA-co-MMA ₅₀	11 700	1.88	4460	7490	1.87	
BIB1EMA-co-MMA ₁₀₀	27 360	2.08	8270	12 700	1.70	
(BIB1EMA-co-MMA ₅₀)- grad-DMAEMA ₅₀	16 200	1.86	8510	4720	1.41	
(BIB1EMA-co-MMA ₁₀₀)- grad-DMAEMA ₅₀	26 900	2.48	12 000	6720	1.54	
BIB2EMA-co-MMA ₂₅	9450	2.25	1780	10 680	3.89	
BIB2EMA-co-MMA50	15 700	2.67	3800	16 100	2.73	
BIB2EMA-co-MMA ₁₀₀	20 900	2.54	7710	17 800	2.27	

thermolysis took place. This also suggested that the thermolysis occurring with the degradable hyperbranched (co)polymers was the result of the thermolysis of the acylal group in these polymers.

CONCLUSION

Degradable hyperbranched (co)polymers were successfully synthesized via ATRP using a novel degradable inimer bearing acylal groups, synthesized for the purposes of this study. The behavior of this inimer during the polymerization of MMA followed the trends described in the literature. Five hyperbranched polymers were synthesized in total, from which three were hyperbranched homopolymers of MMA with different initial monomer-to-inimer molar ratios, and two were hyperbranched amphiphilic gradient copolymers with different compositions. These hyperbranched amphiphilic copolymers were soluble in THF: water mixtures with water content equal to or less than 50% w/w and exhibited hydrodynamic sizes which increased with the water content in the solvent mixture. Because of the presence of the acylal groups in their main chains, the hyperbranched polymers could be quantitatively thermolyzed to linear polymers. The time necessary for complete thermolysis of the hyperbranched polymers was found to increase with the size of the degradable hyperbranched polymers. No thermolysis was observed for similar hyperbranched polymers synthesized using a nondegradable inimer, isomeric to the degradable one. Future work will employ the present hyperbranched (co)polymers as thermolyzable cores for the preparation of cleavable^{25,55-57} functional polymer conetworks.^{21-24,58}

AUTHOR INFORMATION

Corresponding Author

*E-mail: costasp@ucy.ac.cy.

ACKNOWLEDGMENTS

We thank the Cyprus Research Promotion Foundation and the European Commission's Structural and Cohesion Funds for Cyprus for a Doctoral Research Grant (PENEK2008 ENISX/0308/45) to M.R.-K. Furthermore, we are grateful to the University of Cyprus Research Committee for further funding and to the A. G. Leventis Foundation for financial support in establishing the NMR spectroscopy facilities at the University of Cyprus. Finally, we thank our colleagues Dr. M. Vamvakaki

and Mr. P. Falireas (University of Crete), and Dr. K. S. Pafiti (University of Cyprus) for performing for us additional DLS experiments.

REFERENCES

- (1) Hult, A.; Johansson, M.; Malmström, E. Adv. Polym. Sci. 1999, 143, 1-34.
- (2) Mori, H.; Müller, A. H. E. Top. Curr. Chem. 2003, 228, 1-37.
- (3) Yates, C. R.; Hayes, W. Eur. Polym. J. 2004, 40, 1257-1281.
- (4) Voit, B. I.; Lederer, A. Chem. Rev. 2009, 109, 5924-5973.
- (5) Voit, B. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 2505–2525.
- (6) Voit, B. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 2679–2699.
- (7) Laibinis, P. E.; Whitesides, G. M. J. Am. Chem. Soc. 1992, 114, 9022–9028.
- (8) Zhou, Y.; Bruening, M. L.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. *Langmuir* **1996**, *12*, 5519–5521.
- (9) Zhao, M.; Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. Langmuir **1997**, *13*, 1388–1391.
- (10) Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. J. Am. Chem. Soc. **1996**, 118, 3773–3774.
- (11) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770–778.
- (12) Johansson, M.; Malmström, E.; Hult, A. J. Polym. Sci., Part A: Polym. Chem. 1993, 31, 619-624.
- (13) Shi, W. F.; Rånby, B. J. Appl. Polym. Sci. 1996, 59, 1937-1944.
- (14) Shi, W. F.; Rånby, B. J. Appl. Polym. Sci. 1996, 59, 1945-1950.
- (15) Shi, W. F.; Rånby, B. J. Appl. Polym. Sci. 1996, 59, 1951-1956.
- (16) Claesson, H.; Malmström, E.; Johansson, M.; Hult, A.; Doyle,
- M.; Månson, J.-A. E. Prog. Org. Coat. 2002, 44, 63-67.
- (17) Uhrich, K. Trends Polym. Sci. 1997, 5, 388-393.
- (18) Roberts, J.; Bhalgat, M.; Zera, R. J. Biomed. Mater. Res. 1996, 30, 53-65.

(19) Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. J. Polym. Sci., Part A: Polym. Chem. **1996**, 34, 1359–1363.

(20) Zhang, Y.; Wada, T.; Sasabe, H. Polymer 1997, 38, 2893-2897.

(21) Gudipati, C. S.; Greenlief, C. M.; Johnson, J. A.; Prayongpan, P.; Wooley, K. L. J. Polym. Sci., Part A: Polym. Chem. 2004, 42, 6193– 6208

(22) Bartels, J. W.; Cheng, C.; Powell, K. T.; Xu, J.; Wooley, K. L. Macromol. Chem. Phys. 2007, 208, 1676–1687.

- (23) Lin, C.; Gitsov, I. Macromolecules 2010, 43, 10017-10030.
- (24) Lin, C.; Gitsov, I. Macromolecules 2010, 43, 3256-3267.

(25) Bencherif, S. A.; Sheehan, J. A.; Hollinger, J. O.; Walker, L. M.; Matyjaszewski, K.; Washburn, N. R. J. Biomed. Mater. Res.: Part A 2009, 90, 142–153.

(26) (a) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. Macromolecules 1996, 29, 1079–1081. (b) Matyjaszewski, K.; Gaynor, S. G. Macromolecules 1997, 30, 7042–7049. (c) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. Macromolecules 1997, 30, 5192–5194. (d) Matyjaszewski, K.; Gaynor, S. G.; Müller, A. H. E. Macromolecules 1997, 30, 7034–7041. (e) Matyjaszewski, K.; Pyun, J.; Gaynor, S. G. Macromol. Rapid Commun. 1998, 19, 665–670. (f) Yoon, J. A.; Young, T.; Matyjaszewski, K.; Kowalewski, T. ACS Appl. Mater & Interfaces 2010, 2, 2475–2480. (g) Matyjaszewski, K.; Xia, J. Chem. Rev. 2001, 101, 2921–2990.

- (27) Weimer, W. M.; Frechet, J. M.; Gitsov, I. J. Polym. Sci., Part A: Polym. Chem. **1998**, 36, 955–970.
- (28) Cheng, C.; Wooley, K. L.; Khoshdel, E. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 4754–4770.
- (29) Du, W.; Nystrom, A. M.; Zhang, L.; Powell, K. T.; Li, Y.; Cheng, C.; Wickline, S. A.; Wooley, K. L. *Biomacromolecules* **2008**, *9*, 2826–2833.
- (30) Percec, V.; Barboiu, B.; Grigoras, C.; Bera, T. K. J. Am. Chem. Soc. 2003, 125, 6503-6516.
- (31) Tsarevsky, N. V.; Huang, J.; Matyjaszewski, K. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 6839–6851.

(32) Isaure, F.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C.; Armes, S.; Bütün, V. Chem. Commun. 2004, 1138–1139.

Macromolecules

- (33) Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, H. Y. *Macromolecules* **2003**, *36*, 7446–7452.
- (34) Carter, S.; Hunt, B.; Rimmer, S. Macromolecules 2005, 38, 4595-4603.
- (35) Rimmer, S.; Carter, S. R.; Rutkaite, R.; Haycock, J. W.; Swanson, L. Soft Matter 2007, 3, 971–973.
- (36) Carter, S. R.; England, R. M.; Hunt, B.; Rimmer, S. *Macromol. Biosci.* **2007**, *7*, 975–986.
- (37) Ishizu, K.; Kojima, T.; Ohta, Y.; Shibuya, T. J. Colloid Interface Sci. 2004, 272, 76–81.
- (38) Isaure, F.; Cormack, P. A. G.; Sherrington, D. C. *Macromolecules* **2004**, 37, 2096–2105.
- (39) Baudry, R.; Sherrington, D. C. Macromolecules 2006, 39, 1455–1460.
- (40) Baudry, R.; Sherrington, D. C. Macromolecules 2006, 39, 5230-5237.
- (41) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. J. Am. Chem. Soc. **1995**, 117, 10763–10764.
- (42) Tao, Y.; He, J.; Wang, Z.; Pan, J.; Jiang, H.; Chen, S.; Yang, Y. *Macromolecules* **2001**, *34*, 4742–4748.
- (43) Li, C.; He, J.; Li, L.; Cao, J.; Yang, Y. Macromolecules **1999**, *32*, 7012–7014.
- (44) Niu, A.; Li, C.; Zhao, Y.; He, J.; Yang, Y.; Wu, C. *Macromolecules* **2001**, *34*, 460–464.
- (45) Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083.
- (46) Bütün, V.; Bannister, I.; Billingham, N. C.; Sherrington, D. C.; Armes, S. P. *Macromolecules* **2005**, *38*, 4977–4982.
- (47) Simon, P. F. W.; Radke, W.; Müller, A. H. E. Macromol. Rapid Commun. 1997, 18, 865–873.
- (48) Simon, P. F. W.; Müller, A. H. E.; Pakula, T. Macromolecules 2001, 34, 1677–1684.
- (49) Simon, P. F. W.; Müller, A. H. E. Macromolecules 2001, 34, 6206-6213.
- (50) Bally, F.; Ismailova, E.; Brochon, C.; Serra, C. A.; Hadziioannou, G. *Macromolecules* **2011**, *44*, 7124–7131.
- (51) von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3831–
- 3833. (52) Mori, H.; Seng, C. D.; Lechner, H.; Zhang, M.; Müller, A. H. E. *Macromolecules* **2002**, 35, 9270–9281.
- (53) Yan, D.; Müller, A. H. E.; Matyjaszewski, K. Macromolecules 1997, 30, 7024–7033.
- (54) Choucair, A.; Eisenberg, A. Eur. Phys. J. 2003, 10, 37-44.
- (55) Themistou, E.; Kanari, A.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 5811–5823.
- (56) Themistou, E.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 5853–5870.
- (57) (a) Rikkou-Kalourkoti, M.; Loizou, E.; Porcar, L.; Matyjaszewski, K.; Patrickios, C. S. Polym. Chem. 2012, 3, 105–116.
 (b) Rikkou, M. D.; Loizou, E.; Porcar, L.; Butler, P.; Patrickios, C. S. Macromolecules 2009, 42, 9412–9421. (c) Rikkou, M. D.; Patrickios, C. S. Macromolecules 2008, 41, 5957–5959. (d) Themistou, E.; Patrickios, C. S. Macromol. Chem. Phys. 2008, 209, 1021–1028.
 (e) Themistou, E.; Patrickios, C. S. Macromolecules 2007, 40, 5231– 5234. (f) Kafouris, D.; Themistou, E.; Patrickios, C. S. Chem. Mater. 2006, 18, 85–93. (g) Themistou, E.; Patrickios, C. S. Macromolecules 2004, 37, 6734–6743.
- (58) (a) Pafiti, K. S.; Philippou, Z.; Loizou, E.; Porcar, L.; Patrickios, C. S. Macromolecules 2011, 44, 5352–5362. (b) Pafiti, K. S.; Loizou, E.; Patrickios, C. S.; Porcar, L. Macromolecules 2010, 43, 5195–5204. (c) Rikkou, M. D.; Kolokasi, M.; Matyjaszewski, K.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 1878–1886. (d) Rikkou, M. D.; Loizou, E.; Porcar, L.; Patrickios, C. S. Eur. Polym. J. 2010, 46, 441–449. (e) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 4289–4301. (f) Hadjiantoniou, N. A.; Patrickios, C. S.; Thomann, Y.; Tiller, J. C. Macromol. Chem. Phys. 2009, 210, 942–950. (g) Kafouris, D.;

Gradzielski, M.; Patrickios, C. S. Macromolecules 2009, 42, 2972-2980. (h) Achilleos, M.; Legge, T. M.; Perrier, S.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 7556-7565. (i) Triftaridou, A. I.; Loizou, E.; Patrickios, C. S. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 4420-4432. (j) Georgiou, T. K.; Patrickios, C. S. Biomacromolecules 2008, 9, 574-582. (k) Vamvakaki, M.; Patrickios, C. S. Soft Matter 2008, 4, 268-276. (1) Hadjiantoniou, N. A.; Patrickios, C. S. Polvmer 2007, 48, 7041-7048. (m) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. Langmuir 2007, 23, 10746-10755. (n) Vamvakaki, M.; Patrickios, C. S.; Lindner, P.; Gradzielski, M. Langmuir 2007, 23, 10433-10437. (o) Achilleos, M.; Krasia-Christoforou, T.; Patrickios, C. S. Macromolecules 2007, 40, 5575-5581. (p) Triftaridou, A. I.; Vamvakaki, M.; Patrickios, C. S. Biomacromolecules 2007, 8, 1615-1623. (q) Georgiou, T. K.; Patrickios, C. S.; Groh, P. W.; Iván, B. Macromolecules 2007, 40, 2335-2343. (r) Kali, G.; Georgiou, T. K.; Iván, B.; Patrickios, C. S.; Loizou, E.; Thomann, Y.; Tiller, J. C. Macromolecules 2007, 40, 2192-2200. (s) Triftaridou, A. I.; Kafouris, D.; Vamvakaki, M.; Georgiou, T. K.; Krasia, T. C.; Themistou, E.; Hadjiantoniou, N.; Patrickios, C. S. Polym. Bull. 2007, 58, 185-190. (t) Achilleos, D. S.; Georgiou, T. K.; Patrickios, C. S. Biomacromolecules 2006, 7, 3396-3405. (u) Karbarz, M.; Stojek, Z.; Georgiou, T. K.; Patrickios, C. S. Polvmer 2006, 47, 5182-5186. (v) Krasia, T. C.; Patrickios, C. S. Macromolecules 2006, 39, 2467-2473. (w) Georgiou, T. K.; Patrickios, C. S. Macromolecules 2006, 39, 1560-1568. (x) Karbarz, M.; Stojek, Z.; Patrickios, C. S. Polvmer 2005, 46, 7456-7462. (y) Georgiou, T. K.; Vamvakaki, M.; Patrickios, C. S. Polymer 2004, 45, 7341-7355. (z) Loizou, E.; Triftaridou, A. I.; Georgiou, T. K.; Vamvakaki, M.; Patrickios, C. S. Biomacromolecules 2003, 4, 1150-1160.