Synthesis of Hyperbranched and Highly Branched Methacrylates by Self-Condensing Group Transfer Copolymerization

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ABSTRACT: We report a study of the self-condensing group transfer copolymerization of the initiator−monomer (“inimer”) 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (MTSHEMA) with methyl methacrylate (MMA). The highly branched polymethacrylates were characterized by multidetector SEC and NMR. Kinetic measurements show that cyclization, i.e., the intramolecular reaction of an active center with the vinyl group of the polymer, limits the molecular weights and lowers the polydispersity. Depending on the comonomer ratio, $\gamma = [\mathrm{MMA}]_0/[\mathrm{MTSHEMA}]_0$, molecular weights up to $M_w = 240\,000$ at a polydispersity of $M_w/M_n \approx 3$ could be obtained. The Mark−Houwink exponent of these branched copolymers depends on the comonomer ratio and is significantly lower ($0.45 \geq \alpha \geq 0.23$) than linear PMMA ($\alpha = 0.69$). Only 4% of inimer are necessary to lower the Mark−Houwink exponent to half the value of linear PMMA. Using slow addition of the comonomer mixture to the monofunctional initiator 1-methoxy-3-(trimethylsilyloxy)-2-methyl-1-propene (MTS) enables control of the molecular weights and decreases the polydispersity to $M_w/M_n \approx 1.6$. Copolymerization of MTSHEMA with *tert*-butyl methacrylate followed by acid-catalyzed hydrolysis of the *tert*-butyl groups yields highly branched poly(methacrylic acid).

Introduction

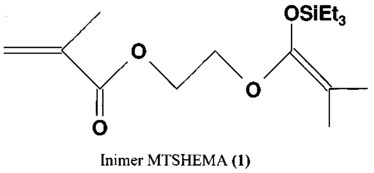
In the past decade, interest in hyperbranched polymers has risen. They combine some features of dendrimers, e.g., an increasing number of end groups and a compact structure in solution with the ease of preparation of linear polymers by means of a one-pot reaction.

Traditionally, hyperbranched polymers have been prepared by polycondensation reactions of AB_2 monomers.[1] However, vinyl monomers cannot be polymerized by that approach. This drawback was overcome by self-condensing vinyl polymerization (SCVP) of initiator−monomers having the general structure AB*, where A stands for a double bond and B* represents an initiating group.[2] Thus, these molecules combine features of an initiator and a monomer and have therefore been named “inimer”.[3−6] This approach has been applied to various types of living polymerization, i.e., cationic,[2] ATRP,[7,8] nitroxide-mediated radical polymerizations,[9] and even ring-opening polymerization.[10] Independently, we[11,12] and Sakamoto et al.[13] have used group transfer polymerization (GTP) of the inimer MTSHEMA (**1**) (cf. Chart 1) where the silyl ketene acetal group can be activated by nucleophilic catalysts to initiate GTP.

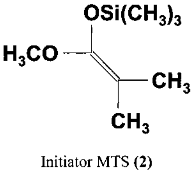
Group transfer polymerization offers the possibility to perform a controlled polymerization of methacrylates at room temperature.[14] Careful choice of the catalyst used to activate the initiator can furthermore fine-tune the polymerization rate. Besides the bifluoride anion, the group of oxyanions are important GTP catalysts because of their relative ease in preparation as well in usage.[15]

Self-condensing vinyl copolymerization (SCVCP) of AB* monomers with conventional monomers, M, leads to highly branched polymers, allowing for the control of molecular weight distribution and degree of branching.[6,7,10,16−20] Alternatively, these copolymers can be prepared via SCVP of “macroinimers”,[4,21−23] i.e., heterotelechelic macromolecules possessing both an initiating and a polymerizable moiety. Both processes permit control of the molecular weight distribution as well as the degree of branching, DB. Depending on the chemical nature of the comonomer, different types of functional groups can be incorporated into the polymer. Because the number of linear units is higher the degree of branching, DB, of the copolymers is lower than that of SCVP homopolymers. However, the effect on solution properties like intrinsic viscosity and radius of gyration should be less than proportional, because branched polymers—above a limiting molecular weight—are self-similar objects.[24] Therefore, a copolycondensation or copolymerization is an economic approach to obtain highly branched polymers, especially when aiming at controlling rheology.

Chart 1



Inimer MTSHEMA (**1**)



Initiator MTS (**2**)

Molecular weights in SCVP as well as in SCVCP are limited by the cyclization reaction in which an active center reacts intramolecularly with the double bond, forming a polyfunctional macroinitiator containing one loop. Clearly, this loop should only have a minor effect on the physical properties, but its presence will significantly decrease the polydispersity of the polymer formed.[25,26] As pointed out by some recent theoretical and experimental work,[26−29] the presence of an *f*-

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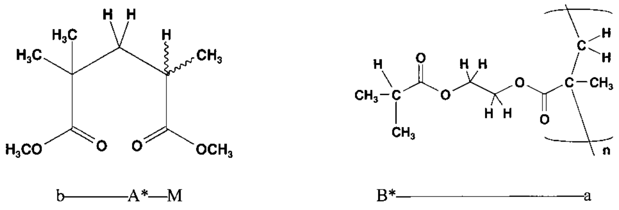
Chart 2



(3) PIBHEMA

functional initiator, G_f, which only contains initiating B* moieties, should furthermore increase the control over the molecular weight distribution and degree of branching, DB. Recent calculations show that the use of an *f*-functional initiator will have a significant effect on the molecular weight distribution in SCVCP, too.[30,31] Furthermore, the use of an *f*-functional initiator which only contains initiating B* moieties should lead to polymers with narrow MWD and higher degree of branching, DB, if the AB* monomer is added slowly (semibatch conditions).[17,27,32] In GTP, 1-methoxy-3-(trimethylsilyloxy)-2-methyl-1-propene (MTS) (**2**) can serve as a monofunctional initiator (Chart 1).

This paper describes results of the self-condensing group transfer copolymerization (SCVCP) of the inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (MTSHEMA, **1**) with methyl methacrylate (MMA) and *tert*-butyl methacrylate (*t*BMA). We demonstrate that SCVCP using slow monomer addition and the commonly used monofunctional GTP initiator MTS (**2**) can be employed to obtain highly branched polymers in a controlled manner.

Experimental Section

NMR Spectra. ^{1}H NMR spectra were recorded at 200 and 400 MHz in $CDCl_3$ on Bruker AC-200 or AM-400 spectrometers using the solvent signal ($\delta = 7.26$ ppm) as an internal standard. Tacticities are described as follows: m, meso; r, racemic.

Materials. Tetrahydrofuran (THF, BASF GmbH, 99.5+%) was distilled over a 1 m column and dried over potassium. After degassing, the solvent was stirred over sodium/potassium alloy and distilled in vacuo prior to use. Methyl methacrylate (MMA, BASF GmbH, 99.5+%) and *tert*-butyl methacrylate (*t*BMA, BASF GmbH, 99.5+%) were distilled over a 1 m column filled with Sulzer packing at 45 mbar. After degassing, the distillate was stirred over CaH_2 (Aldrich, 99.99%), degassed and distilled in high vacuum. Perdeuterated methyl methacrylate (MMA-d_8, kindly supplied by Prof. Dr. M. Stamm, Max-Planck Institute for Polymer Research, Mainz, Germany, 99.9+%) was stabilized using IRGANOX 1010 (Ciba-Geigy, 99+%), stirred over CaH_2 (Aldrich, 99.99%) and filtered through a 2 cm Al_2O_3 column (ICN Alumina B, Akt. I, ICN Biomedicals GmbH) prior to use. 2,2′-Azobisisobutyrolnitrile (Aldrich, 98%), acetic acid (96 wt %, Acros, p.a.), diethyl ether (Fluka, purum; ≥99.0%), dioxane (Fluka, purum ≥98.0%), ethyl acetate (Acros, p.a.), methanol (BASF GmbH, 99+%), hydrobromic acid (48 wt % solution in water, Acros, tech.), tetrabutylammonium fluoride (1 M solution in THF, Aldrich,) were used without prior purification. The GTP catalysts tetrabutylammonium bibenzoate[15] (TBABB), tetrabutylammonium bi(3-chlorobenzoate)[15] (TBAB3ClB), tris(dimethylamino)sulfonium bifluoride[33] ($TASHF_2$) and the inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate[12,13] (MTSHEMA) (**1**) were prepared according to known procedures. 1-Methoxy-3-(trimethylsilyloxy)-2-methyl-1-propene (**2**) (MTS, ABCR, 99.9+%) was distilled under reduced pressure using a split-tube column and stored under high vacuum. 2,2,4-Trimethyl glutaric acid dimethyl ester (**3**) (see Chart 2) was kindly supplied by Dr. L. Lochmann, Prague.[34,35] ^{1}H NMR (400 MHz) δ/ppm: 3.50 (s, 6 H, OCH_3); 2.43 (qdd, 1 H, H_3-COOC(CH_3)$H \equiv$ A* group); 2.03 (dd, 1 H, $^2J = 14.2$ Hz, $^3J = 8.8$ Hz, C*H*H); 1.56 (dd, 1 H, $^2J = 14.2$ Hz, $^3J = 3.9$ Hz,CH*H*); 1.10 (d, 3 H, H_3COOC(CH_3)H)); 1.09 and 1.07 (s, 3 H each, C(CH_3)$_2$).

Kinetic Experiments. All kinetic experiments were performed in a stirred tank reactor under nitrogen atmosphere in THF. Polymerization was started by adding the catalyst to the comonomer mixture. The reaction conditions are outlined in Table 1. The polymerization was quenched with a methanol/acetic acid/tetrabutylammonium fluoride mixture (9:1:1) After evaporation of the solvent, the polymer was dissolved in benzene, filtered, and freeze-dried. The conversion of both comonomers (MTSHEMA and MMA) was monitored by gas chromatography using octane as internal standard. Samples of 10 μL were injected at a temperature of 120 °C on a Fisons GC 8000 system. A Megabore methylpolysiloxane capillary column DB1 (length 30 m, 0.53 mm i.d., film thickness 1.5 μm) was employed as stationary phase, with hydrogen as the mobile phase. Separation was performed following a temperature ramp (50 °C for 4 min and then heating to 150 °C a rate of 20 °C/min and keeping the temperature for additional 5 min). The sample was finally analyzed with a FID operating at 170 °C. Raw data were recorded and evaluated using the ChromCard for Windows Software V1.17β.

Copolymerization of MTSHEMA with MMA. Polymerizations were performed at room temperature at a constant TBABB and MTSHEMA (**1**) concentration varying the concentration of MMA. In a typical experiment, the polymerization was started by the addition of 0.25 mL of a TBABB solution in THF ($c = 1.92 \times 10^{-3}$ mol L^{-1}; $C_0 = 7.64 \times 10^{-6}$ mol L^{-1}) to a mixture of 0.30 g of MTSHEMA (**1**) ($I_0 = 0.019$ mol L^{-1}) and 8.16 g of MMA ($M_0 = 1.63$ mol L^{-1}) in 50 mL of THF. At all comonomer ratios, γ = [MMA]/[MTSHEMA] (cf. Table 2), full conversion of both comonomers was reached after 20 min. The polymerization was quenched with few drops of a methanol/acetic acid/tetrabutylammonium fluoride mixture (9:1:1) After evaporation of the solvent, the polymer was dissolved in benzene, filtered, and freeze-dried.

Copolymerization under Semibatch Conditions. Polymerizations were performed at room temperature at constant TBABB, MTSHEMA (**1**), and MMA concentrations while varying the concentration of MTS (**2**). A mixture of 0.41 g of MTSHEMA (**1**) ($I_0 = 0.03$ mol L^{-1}) and 3.26 g of MMA ($M_0 = 0.73$ mol L^{-1}) in 45 mL of THF and a solution of 0.91 mL of TBABB ($c = 1.92 \times 10^{-3}$ mol L^{-1} in THF; $C_0 = 5.48 \times 10^{-5}$ mol L^{-1}) in 32 mL of THF were added separately but simultaneously under vigorous stirring over 45 min to a solution of 0.17 g of MTS (**2**) ($G_0 = 0.1$ mol L^{-1}) in 10 mL of THF. For all experiments, full conversion of both comonomers was reached after additional 20 min. The polymerization was quenched with few drops of a methanol/acetic acid/tetrabutylammonium fluoride mixture (9:1:1) After evaporation of the solvent, the polymer was dissolved in benzene, filtered, and freeze-dried.

Copolymerization of MTSHEMA and *t*BMA. Copolymerization of *t*BMA with MTSHEMA (**1**) was achieved under $TASHF_2$ catalysis in THF at room temperature. In a typical experiment, the copolymerization was performed by the dropwise addition of a mixture of 20 mL of $TASHF_2$ ($c = 9.8 \times 10^{-4}$ mol L^{-1} in THF; $C_0 = 4.9 \times 10^{-5}$ mol L^{-1}) in 20 mL of THF to a mixture of 0.75 g of MTSHEMA (**1**) ($I_0 = 0.02$ mol L^{-1}) and 8.16 g of *t*BMA ($M_0 = 0.50$ mol L^{-1}) in 120 mL of THF. At all comonomer ratios, γ, full conversion was reached after 60 min. The polymerization was quenched with few drops of a methanol/acetic acid mixture (9:1). The polymer was precipitated in methanol and dried in vacuo for 24 h at 40 °C.

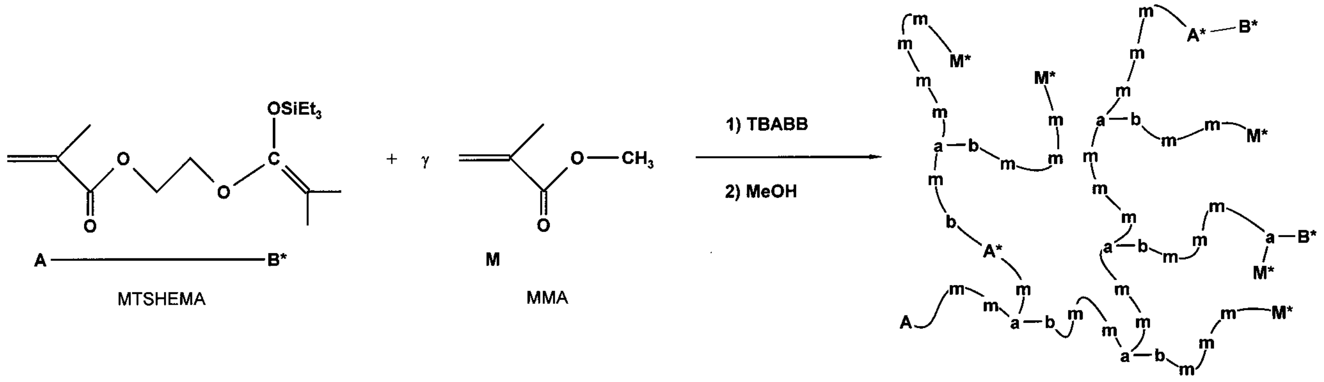
Preparation of Branched Poly(methacrylic acid sodium salt) via Hydrolysis of Branched P*t*BMA. Branched P*t*BMA (2 g; 72 000 mol of *t*BMA groups) was dissolved in a dioxane/methanol = 9/1 mixture. Hydrobromic acid (10 mL) was added and the mixture was refluxed for 24 h. The resulting poly(methacrylic acid) was precipitated in diethyl ether, redissolved in dilute aqueous sodium hydroxide solution

Table 1. Experimental Conditions, Molecular Weight Averages, and Mark–Houwink Exponents, α, (THF, 25 °C) in the Self-Condensing Group Transfer Copolymerization of MTSHEMA (1) and MMA at a Constant Comonomer Ratio, $\gamma = [\mathrm{MMA}]_0/[\mathrm{MTSHEMA}]_0 = 25$, Where I_0, C_0 Are Initial Concentrations of Inimer and Catalyst, respectively, and x_{MMA} Is Conversion of MMA

symbol	catalyst	$10^3 I_0$/mol L^{-1}	$10^6 C_0$/mol L^{-1}	T/°C	x_{MMA}	$10^4 M_{\mathrm{n}}$	$10^4 M_{\mathrm{w}}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$	α
+	TBAB3ClB[a]	8.41	3.22	20	0.07	0.76	1.85	2.43	0.30
					0.17	0.90	2.40	2.67	0.33
					0.94	1.16	3.56	3.07	0.33
○	TBAB3ClB[a]	8.38	16.8	20	0.96	1.30	3.96	3.05	0.34
					1	1.23	3.94	3.20	0.33
					1	1.11	3.78	3.41	0.28
●	TBABB[b]	8.38	3.22	−20	0.69	1.72	5.56	3.23	0.33
					0.97	1.94	6.73	3.47	0.33
					1	1.89	6.93	3.67	0.32
■	TBABB[b]	8.38	3.22	20	0.91	1.78	6.61	3.71	0.31
					0.99	1.74	6.32	3.63	0.34
					0.99	1.71	6.52	3.81	0.32
▲	TBABB[b]	8.38	1.68	0	0.97	1.78	6.80	3.82	0.30
					1	1.74	6.73	3.87	0.30
					1	1.75	6.80	3.89	0.30
△	TBABB[b]	8.38	1.68	20	0.825	1.74	6.79	3.90	0.31
					0.975	1.68	6.96	4.14	0.30
					0.996	1.68	7.06	4.20	0.31
▽	TBABB[b]	1.65	0.64	20	0.227	0.92	2.56	2.78	0.33
					0.398	1.04	3.17	3.05	0.32
					0.571	1.14	3.78	3.32	0.30
◇	TBABB[b]	3.35	12.9	20	1	2.45	7.38	3.01	0.34
					1	2.24	7.26	3.24	0.37
					1	2.41	7.46	3.10	0.38
×	TASHF$_2$[c]	8.41	3.22	20	0.447	1.78	5.30	2.98	0.33
					0.527	1.67	5.77	3.46	0.33
					0.639	1.87	6.22	3.33	0.31

[a] Tetrabutylammonium bis(3-chlorobenzoate). [b] Tetrabutylammonium bibenzoate. [c] Tris(dimethylamino)sulfonium bifluoride.

Scheme 1. General Route to Highly Branched Poly(methyl methacrylate)



and precipitated in methanol. Freeze-drying from water yielded a white polymer (yield 75%).

Preparation of Linear Reference Polymers. Linear PMMA and P*t*BMA with various molecular weights were prepared by conventional free radical polymerization of the corresponding monomers in ethyl acetate, varying the amount of initiator. A typical polymerization was performed by stirring a mixture of 0.02 g of 2,2′-azobisisobutyrolnitrile (0,12 mmol) and 3 g of *t*BMA (21,1 mmol) in 30 mL of degassed ethyl acetate at 85 °C for 36 h. The crude polymer was precipitated in methanol and dried in vacuo for 24 h at 40 °C. Molecular weights for this example (determined by universal calibration): $M_{\mathrm{n}} = 66\,800$, $M_{\mathrm{w}} = 125\,800$; $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.88$. Mixtures of different molecular weights were used as comparison in the solution viscosity studies. Linear PIBHEMA as reference material for NMR studies[13] was prepared according to the literature.[12] ^{1}H NMR (200 MHz), δ/ppm: 4.1−3.7 (OCH_2CH_2O); 2.32 ((C═O)C(CH$_3$)H ≡ B* group); 1.67 (CH_2, m); 1.57 (CH_2, r); 1.08 (CH_3, mm); 0.94 ((C═O)C(CH_3)H); 0.79 (CH_3, mr); 0.62 (CH_3, mm).

SEC Characterization. SEC measurements were performed in THF at room temperature using 5 μm PSS SDVgel columns (10^3, 10^5, 10^6 Å, 30 cm each; Polymer Standards Service, Mainz, Germany) at a flow rate of 0.5 mL/min. A Viskotek viscosity detector H 502B (operating at 30 °C), a Shodex RI-71 refractive index detector; a DAWN DSP F multiangle laser light scattering photometer ($l_0 = 632.8$ nm; 10 scattering angles from 35.4 to 144.6° were evaluated), and an Applied Biosystems 1000S UV diode array detector were used. The refractive index increment d*n*/d*c* was determined on-line using an NFT Scan-Ref interferometer (Nanofilm Technology, Göttingen, Germany) operating at a laser wavelength of $l_0 = 632.8$ nm. Raw data were processed using PSS-WinGPC V4.02 and NFT V2.0c software.

Universal calibration curves,[36−38] $[\eta]M = f(V_{\mathrm{e}})$, were constructed using narrow PMMA standards of different molecular weights in THF. Since this universal calibration curve is valid for any polymer structure, absolute molecular weights can be determined by this method within an error range of 10%.

Results and Discussion

The general synthetic route of the self-condensing copolymerization of MTSHEMA and MMA leading to highly branched polymers is outlined in Scheme 1 and Table 1. The curved lines represent polymer chains. A*,

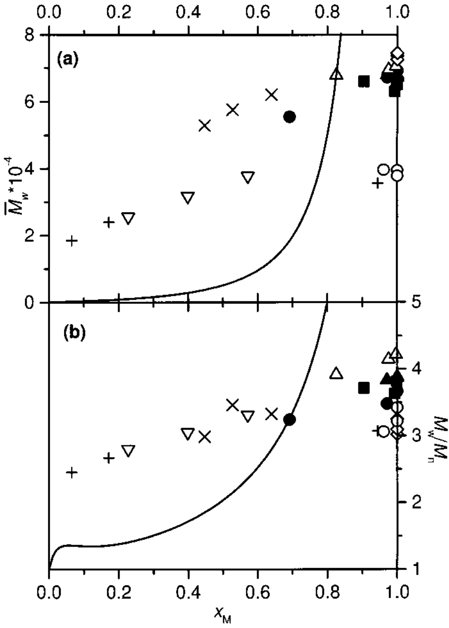


Figure 1. Plot of (a) the weight-average molecular weight, M_w, and (b) the polydispersity index, M_w/M_n vs the conversion of MMA, x_M, for the copolymerization of MTSHEMA (**1**) and MMA (γ = [MMA]$_0$/[MTSHEMA]$_0$ = 25) under different reaction conditions and comparison to theory (—). For reaction conditions and symbols see Table 1.

B*, and M* are active units whereas a, b, and m are reacted ones.

The dependence of the molecular weight distribution on conversion of monomer, x_M, for a batch copolymerization of MTSHEMA (**1**) with MMA was monitored at a constant comonomer ratio, γ = [MMA]$_0$/[MTSHEMA]$_0$ = 25, varying the absolute concentrations of both comonomers, as well as the nature and concentration of catalyst; cf. Table 1. None of the polymers absorbed in the UV at λ = 300 nm, indicating the absence of termination by backbiting.[39] Nevertheless, the evolution of the molecular weights as a function of MMA conversion, x_M, deviates significantly from the theoretical predictions (Figure 1). According to theory[18] (assuming equal reactivity of active centers) a strong increase of M_w with conversion of the comonomer, x_M, can be expected in the limiting case, $\gamma \gg 1$

$$M_w = m_M\left(1 + \frac{\gamma\, x_M}{(1 - x_M)^2}\right) \tag{1}$$

$$\lim_{x_M \to 1} M_w \approx \frac{m_M \gamma}{(1 - x_M)^2}$$

where m_M is the molar mass of the comonomer. According to Figure 1 and Table 1, the molecular weights are lower than predicted by theory. At complete conversion a finite value is reached which is in first approximation is independent of the reaction conditions. For nonequal rate constants the same trend is predicted.[40] The observation of finite molecular weight averages can be explained by the occurrence of the cyclization reaction that was studied theoretically for AB$_2$ polycondensation by Dušek et al.[25] using Monte Carlo simulation, and corroborated very recently by Galina et al.[29] The authors predicted that the fraction of cyclic x-mers would increase with increasing degree of polymerization, P_n, and overall conversion. According to their results, the number- and the weight-average molecular weights do not diverge in the presence of cyclization but remain finite even at complete conversion of the A groups.

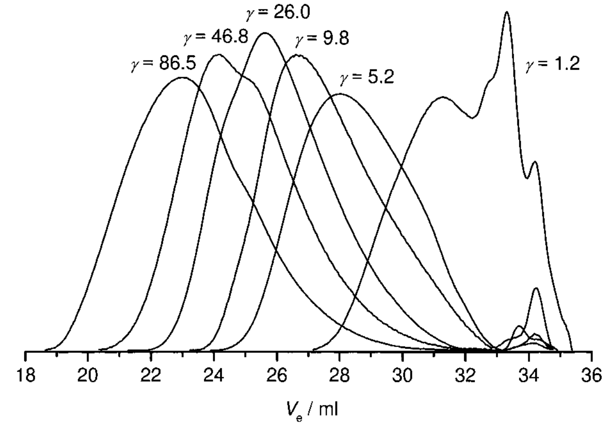


Figure 2. SEC traces of branched copolymers of MTSHEMA and MMA at different comonomer ratios, γ = [MMA]$_0$/[MTSHEMA]$_0$.

Table 2. Molecular Weights and Mark–Houwink Exponents, α, of the Copolymerization of MTSHEMA (1) with MMA at Different Comonomer Ratios, γ = [MMA]$_0$/[MTSHEMA]$_0$, Using Tetrabutylammonium Bibenzoate (TBABB) as Catalyst[c]

symbol	γ	$10^{-3}M_w$[a]	M_w/M_n[a]	α
+	1.2	2.2	3.7	0.21
◇	5.2	13	3.1	0.24
▽	9.8	27	11.3	0.22
△	26.0	67	2.9	0.34
○	46.8	116 103[b]	3.2 1.9[b]	0.41
□	86.5	251 240[b]	3.2 2.3[b]	0.47

[a] Universal calibration. [b] MALLS results. [c] Reaction conditions: initial concentration of MTSHEMA, $I_0 = 2.0 \times 10^{-2}$ mol L^{-1}; initial concentration of catalyst, $C_0 = 7.58 \times 10^{-4}$ mol L^{-1}, room temperature.

Effect of the Comonomer Ratio. The SEC traces of the copolymerization for MTSHEMA (**1**) with MMA for different comonomer ratios, γ, are shown in Figure 2. The elution curves shift toward higher molecular weights with increasing ratio γ.

As the relation between molecular weight and hydrodynamic volume of branched polymers differs substantially from linear ones, absolute molecular weights were established using universal calibration and multiangle laser light scattering (MALLS). The results are given in Table 2. Because of the low signal-to-noise ratio due to the low refractive index increment of the highly branched PMMA, dn/dc = 0.089 mL/g, we were not able to obtain reliable light scattering data for molecular weights M_w < 75 000.

As mentioned before, the molecular weights are limited by the cyclization reaction. Assuming that the ratio of reaction rates of cyclization and chain propagation is independent of comonomer ratio, γ, a relationship between γ and M_n should be linear. Figure 3 shows that the absolute molecular weights at full conversion of MMA agree qualitatively with this assumption; both molecular weight averages increase with the comonomer ratio, γ, whereas the polydispersity index is constant as predicted by theory.

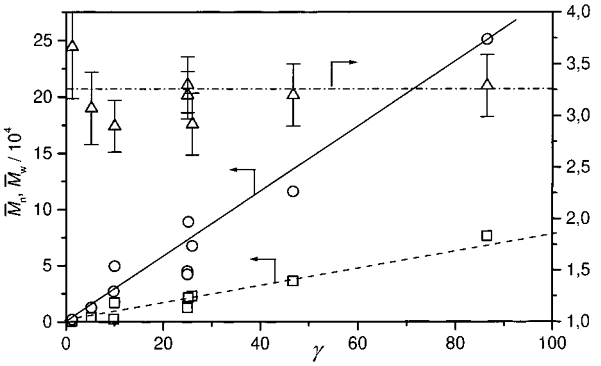


Figure 3. Dependence of molecular weight averages on comonomer ratio, γ = $[MMA]_0/[MTSHEMA]_0$, in the self-condensing group transfer copolymerization of MTSHEMA (**1**) and MMA at complete conversion of MMA ($x_{MMA} \approx 1$): (- -□- -) M_n; (—○—) M_w; (- • -△- • -) M_w/M_n.

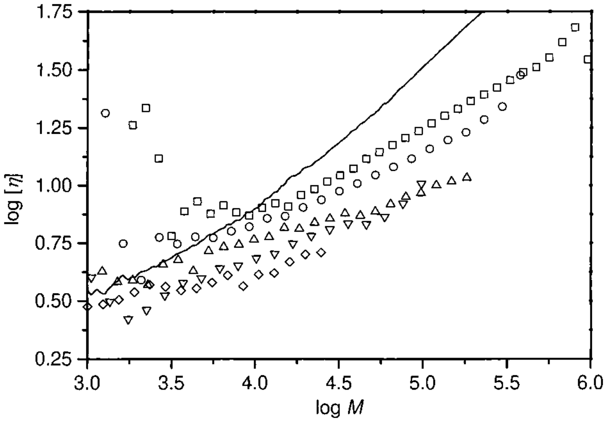


Figure 4. Mark–Houwink plot for the copolymerization of MTSHEMA (**1**) with MMA under different comonomer ratios, $\gamma = [MMA]_0/[MTSHEMA]_0$. Symbols, see Table 2. The viscosity result for PMMA (—) is given for comparison.

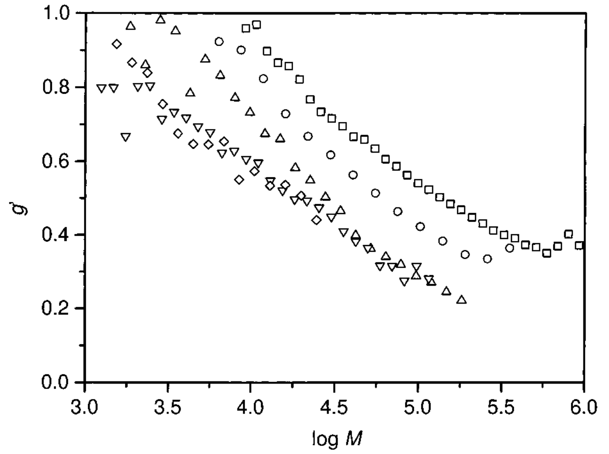


Figure 5. Contraction factors, $g' = [\eta]_{br}/[\eta]_{lin}$, as a function of the molecular weight. Symbols: see Table 2.

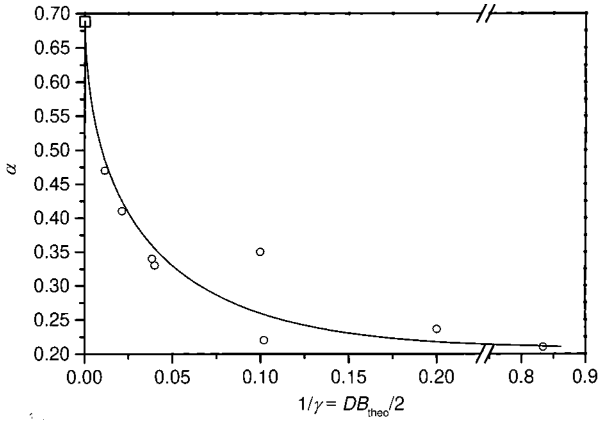


Figure 6. Dependence of the Mark–Houwink exponent, α, on comonomer ratio, $\gamma = [MMA]_0/[MTSHEMA]_0$, for the copolymerization of MTSHEMA (**1**) with MMA. Linear PMMA (⊡): α = 0.68; K = 11.6 mL g^{-1}.

The corresponding Mark–Houwink plots, log $[\eta] = f$ (log M), are presented in Figure 4. The Mark–Houwink exponents, α, are given in Table 2, neglecting data points with molecular weights $M < 10^4$. For $M > 10^4$, the viscosity of the branched polymer is significantly less than that of linear PMMA. The contraction factors,[24,41] $g' = [\eta]_{branched}/[\eta]_{linear}$, decrease with increasing molecular weight for all polymers, which indicates a highly compact structure in solution (Figure 5). Because of the low refractive index increments (vide supra), the radius of gyration could not be determined with sufficient accuracy.

Figure 6 shows the influence of the comonomer ratio, γ, on the Mark–Houwink exponent, α. Even a small amount of MTSHEMA considerably lowers α, leading to a more compact structure in solution than linear PMMA.

Thus, at a comonomer ratio of $\gamma = 26$, (corresponding to only 4% inimer) α is approximately 50% of the value of linear PMMA. Similarly, the melt rheology of branched PMMA is strongly affected even for $\gamma = 26$.[20]

Degree of Branching. According to the theory of the self-condensing vinyl copolymerization[18] the comonomer ratio, γ, can be directly related to the degree of branching, DB_{theo}. Assuming equal reactivity of all active centers, one obtains at full monomer conversion

$$DB_{theo} = \frac{2(1 - e^{-(\gamma+1)})(\gamma + e^{-(\gamma+1)})}{(\gamma + 1)^2} \qquad (2a)$$

If the reactivities of the various active centers are not equal, the dependences are more complex and DB may be higher or lower.[40] However, for the limiting case of high comonomer ratios, $\gamma \gg 1$, the relation becomes very simple and does not depend on the reactivity ratios

$$DB_{theo} \approx 2/\gamma \qquad (2b)$$

To experimentally determine the degree of branching, DB, copolymers of MTSHEMA (**1**) and MMA-d_8 terminated with protons were analyzed by ^{1}H NMR spectroscopy. In the corresponding copolymers, linear monomer units, m, are “invisible” and therefore the protons in A*, B*, and M* centers can be detected even at high comonomer ratios, γ.

According to Table 3, the chemical structure of B* centers is different from that of A* and M* centers. To estimate the proton chemical shifts, model compounds were analyzed by ^{1}H NMR. The structural motif of the protonated B* center is found in the polymer PIBHEMA whereas the structure of the protonated A* and M* centers is found in 2,2,4-trimethyl glutaric acid dimethyl ester (**3**), the linear dimer of MMA, cf. Chart 2.

The ^{1}H NMR-spectra of the copolymers show two distinct signals at 2.39 and 2.26 ppm. According to the reference spectra, the former signal group can be attributed to the sum $b = A^* + M^*$ of protonated A* and M* centers, whereas the latter signal is due to the

Table 3. Structural Units in Self-Condensing Group Transfer Copolymerization of MTSHEMA (1) and MMA, Where the Curved Lines Represent Polymer Chains, R′ Represents the B* or b Part of the MTSHEMA Molecule or Polymer, and R Represents the A* Part, Respectively

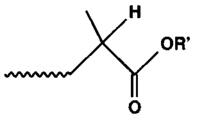
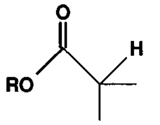
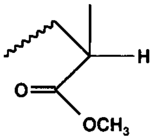
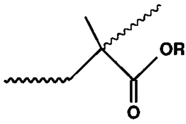
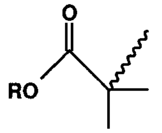
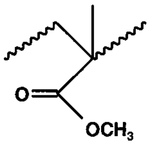
unit, protonated	structure	^{1}H shift/ppm	unit	structure
A*		2.43	a	
B*		2.32	b	
M*		2.43	M	

Table 4. Degree of Branching, DB, for the Copolymerization of MTSHEMA (1) with MMA-d_8 Determined by Eq 2 and by NMR, Respectively

sample	γ	DB$_{\text{theo}}$	DB$_{\text{NMR}}$
CM30	22.6	0.085	0.054
CM31	86	0.023	0.014

protonated B* center. For equal reactivities, the degree of branching, DB$_{\text{NMR}}$, is given as[18]

$$\text{DB}_{\text{NMR}} = 2A^*(1 - A^*) \tag{3}$$

Since A^* cannot be determined independently, we have to estimate it. For equal reactivity of all functional groups, the fraction of A* and M* units can be calculated using the comonomer ratio, γ, and eq 4.[18]

$$A^* = \frac{b}{(1+\gamma)} \tag{4}$$

Insertion into eq 3 leads to

$$\text{DB}_{\text{NMR}} = 2\left(\frac{b}{\gamma+1}\right)\left[1 - \left(\frac{b}{\gamma+1}\right)\right] \tag{5}$$

The results for two copolymerizations of MTSHEMA with MMA-d_8 are given in Table 4.

The degree of branching determined by this approach, DB$_{\text{NMR}}$, agrees qualitatively with the theoretical predictions. However, eqs 2, 4, and 5 are only valid for equal reactivities of active centers (which may not hold in our case) or for $\gamma \gg 1$ (which for strongly differing reactivities is not yet fulfilled for $\gamma = 22.6$, cf. Figure 8 in ref 40). Thus, DB$_{\text{NMR}}$ should be regarded only as a first approximation.

Slow Monomer Addition (Semibatch Polymerization). Defining a comonomer-to-initiator ratio, μ

$$\mu = \frac{M_0 + I_0}{G_0} \tag{6}$$

where M_0, I_0, and G_0 represent the initial concentration of monomer, inimer and initiator, respectively, the expected number-average molecular weight can be expressed as

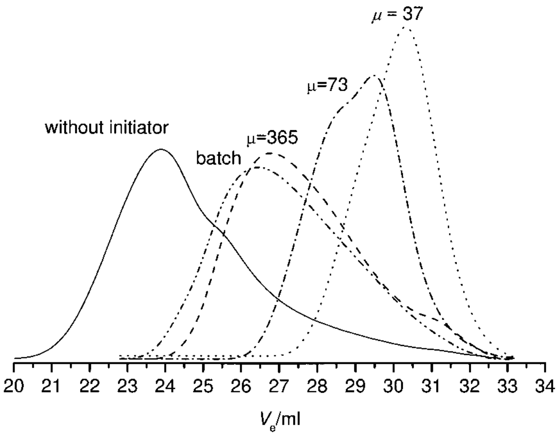


Figure 7. SEC traces of copolymers of MTSHEMA (**1**) and MMA at different ratios of comonomer to initiator and constant comonomer ratio $\gamma = [\text{MMA}]_0/[\text{MTSHEMA}]_0 = 25$.

Table 5. Molecular Weights and Mark–Houwink Exponents, α, for the Self-Condensing Group Transfer Copolymerization of MTSHEMA (1) with MMA in the Presence of the Initiator MTS (2), for Different Comonomer to Initiator Ratios, $\mu = ([\text{MMA}]_0 + [\text{MTSHEMA}]_0)/[\text{MTS}]_0$, at a Constant Comonomer Ratio $\gamma = [\text{MMA}]_0/[\text{MTSHEMA}]_0 = 25$'

μ	symbol	$10^{-3}M_{\text{n,theo}}$	$10^{-3}M_{\text{n}}$^{a}	$10^{-3}M_{\text{w}}$^{a}	$M_{\text{w}}/M_{\text{n}}$^{a}	α
37	□	3.8	4.5	7.2	1.6	0.27
73	○	7.5	7.0	13	1.8	0.27
365	△	38	11	34	3.1	0.30
without initiator	◇		33.2	186 199^b	5.6	0.26
batch	▽		42	139	3.3	0.29

[a] Universal calibration. [b] MALLS results.

$$M_{\text{n,theo}} = \frac{m_{\text{M}}M_0 + m_I I_0}{G_0} \tag{7a}$$

and for $\gamma \gg 1$ the degree of polymerization is

$$P_{\text{n,theo}} = \frac{M_{\text{n,theo}}}{m_{\text{M}}} = \mu \tag{7b}$$

Thus, the comonomer-to-initiator ratio, μ, is the expected degree of polymerization for such a process.

Theoretical calculations predict that SCVP[27,42] and SCVCP[31] using slow inimer addition to an f-functional initiator, G_f, decreases the polydispersity to

$$M_{\text{w}}/M_{\text{n}} \approx 1 + 1/f \tag{8}$$

independent of the absence or presence of comonomer. Figure 7 shows the SEC traces of an experiment where a mixture of MTSHEMA (**1**) and MMA ($\gamma = 25$) and the catalyst solution were added dropwise to the reaction mixture in the presence and the absence of the monofunctional initiator MTS (**2**). In the presence of that initiator, the molecular weight distribution narrows significantly.

The absolute molecular weights and Mark–Houwink exponents determined by universal calibration are given in Table 5. Compared to the batch run without initiator, the use of initiator *and* slow monomer addition permits control of the molecular weight distribution, especially for low ratios of comonomer to initiator, μ. The molecular weight distribution broadens for higher ratios. The effect of the initiator is highlighted when these results are compared to the slow addition of both comonomers

Table 6. Reaction Conditions, Molecular Weights, and Mark−Houwink Exponents, α, for the Copolymerization of MTSHEMA (1) (initial concentration, I_0) with *tert*-butyl Methacrylate, *t*BMA, Using Tris(dimethylamino)sulfonium Bifluoride, TASHF$_2$, as a Catalyst (Initial Concentration, C_0) Where Mark−Houwink Coefficients for Linear P*t*BMA Are[44,45] $\alpha = 0.75$; $K = 4.92$ mL g^{-1}

procedure	symbol	I_0/mol L^{-1}	γ^c	C_0/mol L^{-1}	$10^{-3}\ M_n{}^a$	$M_w/M_n{}^a$	α
batch	☐	0.12	6.6	7.5×10^{-5}	17	2.5	0.29
semibatch without initiator	○	0.02	25	4.9×10^{-5}	36	2.7	0.51
					49^b	2.0^b	

^{a} Universal calibration. ^{b} MALLS results. ^{c} Comonomer ratio $\gamma = [tBMA]_0/[MTSHEMA]_0 = M_0/I_0$.

without added initiator MTS (**2**). In the latter case, the molecular weight distribution is broader and the molecular weights are higher than in the batch run, indicating that molecular weight distribution cannot be controlled by slow monomer addition in the absence of initiator.

Since the rate of monomer/inimer addition cannot be infinitesimally low, inimer molecules may add not only to initiator molecules or to macromolecules generated that way but also to monomer or other inimer molecules leading to polymers with double bonds. This can eventually lead to a broadened bimodal MWD.[27,42] At a constant rate of copolymer addition this reaction will be more pronounced at low initiator concentration (and hence, higher comonomer-to-initiator ratios, μ).

The corresponding Mark−Houwink plots show that all branched polymers have lower viscosities than linear PMMA. There are no significant differences in the Mark−Houwink exponent, α, for different comonomer-to-initiator ratios, μ. As already shown in Figure 6, the increase in the degree of branching, DB, does not strongly affect the Mark−Houwink exponent, α, for higher degrees of branching.

Copolymerization with *tert*-Butyl Methacrylate (*t*BMA). The copolymerization of MTSHEMA (**1**) with *t*BMA yields highly branched P*t*BMA which is a precursor of poly(methacrylic acid), thus opening a facile pathway to highly branched polyelectrolytes. According to Doherty and Müller,[43] a controlled GTP of *t*BMA can be achieved if the catalyst tris(dimethylammonium) bifluoride (TASHF$_2$) is continuously added during the polymerization procedure.

In analogy to the copolymerization with MMA, semibatch reaction conditions in the absence of initiator were used. Reaction parameters, absolute molecular weights (obtained by universal calibration), and the Mark−Houwink exponent of the different copolymers are summarized in Table 6.

The corresponding Mark−Houwink plots (Figure 8) are similar to those in the copolymerization with MMA. Slow addition of both comonomers in the absence of initiator leads to a polymer with a broader molecular weight distribution than in the batch run, although this effect is not as pronounced here. Analogous to the copolymerization with MMA, for a given molecular weight, the corresponding intrinsic viscosity of the polymer is lower than that of linear P*t*MBA, indicating a branched structure.

Acid-catalyzed hydrolysis of the *tert*-butyl groups and neutralization with NaOH produced a water-soluble, highly branched poly(methacrylic acid) sodium salt. Further studies on this interesting highly branched polyelectrolyte will be communicated separately.

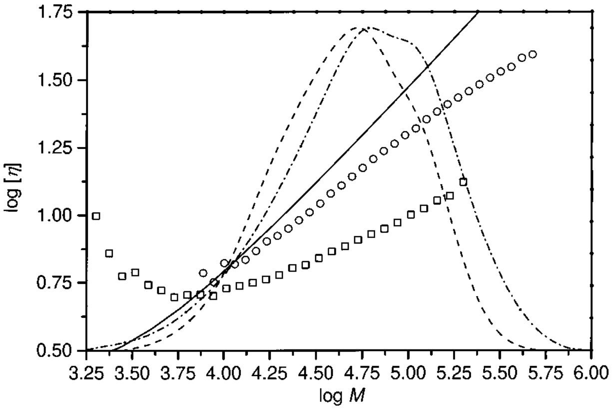


Figure 8. Mark−Houwink plot and RI signals for highly branched Poly(*tert*-butyl methacrylate). Symbol: see Table 6. Key: (—) intrinsic viscosity of linear P*t*BMA; RI signals (- -) batch run and (- • -) semibatch without initiator.

Conclusions

The copolymerization of the inimer MTSHEMA (**1**) with the comonomers MMA and *t*BMA, respectively, leads to hyperbranched and highly branched polymers. As judged from the Mark−Houwink exponents, even small amounts of inimer dramatically decrease the solution viscosity. This is also reflected in our recent results on their melt rheology.[20] Cyclization limits the molecular weights; better control is obtained by slowly adding the comonomers to an added initiator. With added initiator, molecular weights are lower and the molecular weight distribution is more narrow than in a batch run. Furthermore, copolymerization of MTSHEMA with *t*BMA yields highly branched P*t*BMA and, after hydrolysis, a hyperbranched polyelectrolyte.

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