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Polymer Architecture Control in Emulsion Polymerization via Catalytic Chain Transfer Polymerization

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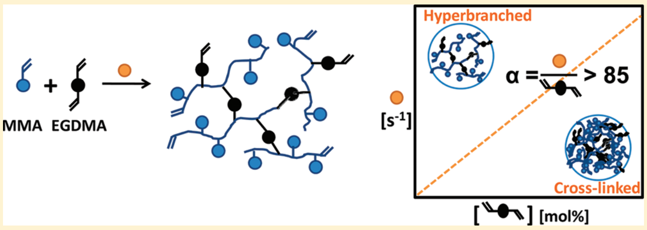
ABSTRACT: Hyperbranched polymers are synthesized via a cobalt(II) mediated emulsion copolymerization of methyl methacrylate and diethylene glycol dimethacrylate. The concentration of divinyl monomer and chain transfer activity have to be balanced in order to prevent gelation of the polymer particles. The physiochemical properties of the cobalt(II) complex, specifically the intrinsic chain transfer activity and the partitioning behavior, play a crucial role in governing the polymer architecture (i.e., branched versus cross-linked). Furthermore, an empirical correlation, based on the chain transfer frequency and the divinyl monomer mol fraction, is presented and validated with the results obtained in emulsion polymerization as well as with available literature data.



INTRODUCTION

Progress in synthetic polymer chemistry has resulted in an array of new routes to synthesize macromolecules with a broad variety of structural architectures, sizes, and functionality. This synthetic diversity has enabled the design of nanostructured polymeric materials for emerging applications such as drug and gene delivery. A particularly attractive class of polymer architectures are dendrimers which exhibit fascinating properties attributed to their structural perfection. However, the elaborate and time-consuming synthesis of these macromolecules has severely limited their technological application. Therefore, focus has shifted to the synthesis of hyperbranched polymers as dendrimer analogues.[1] Hyperbranched polymers can be synthesized in a more economic and facile fashion and, despite being irregular and structurally imperfect macromolecules, possess properties similar to those of dendrimers. Consequently, hyperbranched polymers have found widespread applications in e.g. gene[2−6] and drug[7,8] delivery.

A first synthetic approach to well-defined hyperbranched polymers from free radical polymerization was self-condensing vinyl polymerization (SCVP) which utilizes functional monomers (i.e., inimers).[9] Branching is accomplished by AB_n inimers that contain both a vinyl unsaturation (A group) and an initiating moiety (B group) that allows for further polymerization. Despite being a very effective synthetic tool to synthesize hyperbranched polymers, SCVP suffers from the drawback that special AB_n inimers often have to be synthesized to carry desired initiating groups for cationic polymerization,[9] reversible addition−fragmentation termination polymerization (RAFT),[10,11] nitroxide mediated polymerization (NMP),[12] or atom transfer radical polymerization (ATRP).[13,14] A more generic and facile route to hyperbranched polymers is the free radical polymerization of divinyl monomers in the presence of a chain transfer agent. A first example was the "cascade polymerization" of ethylene glycol dimethacrylate (EGDMA) as reported by Guan.[15] This approach has been extended to copolymerizations of vinyl and divinyl monomers to improve control over the level of branching. This specific synthesis route to hyperbranched polymers is typically referred to as the "Strathclyde methodology" as introduced by Sherrington and co-workers.[16] The main advantage of this methodology is that commercially available reactants are used in a conventional free radical polymerization process. As a consequence, the "Strathclyde methodology" has very recently been used as a tool to synthesize functional and responsive hyperbranched polymers that respond to changes in pH and temperature.[17−19]

Typically, the addition of only minor amounts of cross-linker to a free radical polymerization results in the formation of a cross-linked network and, depending on the concentration, macrogelation. However, the addition of a balancing level of chain transfer agent can prevent network formation and results in the formation of hyperbranched polymers.[16] The principle of the "Strathclyde methodology" was illustrated in 2000 for a copolymerization of methyl methacrylate (MMA) and but-2-ene-1,4-diacrylate (BDA) in the presence of 1-dodecanethiol (DDT).[16] The addition of equimolar amounts of BDA and DDT resulted in the synthesis of hyperbranched polymers. In following years the versatility of the "Strathclyde methodology" was illustrated by varying the molecular structure[20] and functionality of the cross-linker,[21] varying the chain agent and the chain transfer chemistry[17,22−30] and by using dispersed phase polymerization processes.[31,32]

Catalytic chain transfer polymerization (CCTP) is typically used to synthesize linear polymers with a predetermined molecular weight in free radical polymerization.[33−36] Molecular weight control in CCTP is attained when the radical activity of a propagating polymer chain is transferred, via the active cobalt(II) complex, to a monomer molecule. Catalytic chain transfer

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polymerization (CCTP) has also proven to be a promising chemistry for polymer architecture control.[24,29,33] The efficiency of CCTP to synthesize hyperbranched polymers via the "Strathclyde methodology" has been illustrated previously in homogeneous solution polymerization.[24,27] Molecular weight or architecture control by conventional chain transfer agents (e.g., thiols)[16,21,31,32] suffers from their relatively low intrinsic chain transfer activity. Consequently, substantial amounts of thiol are required to inhibit cross-linking. The main advantage of using cobalt(II) complexes as chain transfer agents is the relatively high intrinsic activity combined with the catalytic nature of the chain transfer reaction. This allows for molecular weight control using minimal quantities of catalytic chain transfer agent (CCTA). Furthermore, a specific advantage of utilizing CCTP for controlling the polymer architecture via the "Strathclyde methodology" is that only a pendant vinyl unsaturation remains in the polymer structure, whereas the use of, e.g., thiols introduces potentially adverse organic functionalities.

The synthesis of hyperbranched polymers in dispersed phase polymerization systems is favorable but challenging as the reactants partition between the continuous and dispersed phase. This partitioning behavior affects the concentrations of monomer and chain transfer agent at the locus of polymerization[37] which may affect the branching reaction. Furthermore, the polymerization in principle proceeds as a "bulk polymerization" inside the polymer particles which was expected to favor cross-linking.[38,39] However it has been illustrated that the "Strathclyde methodology" can be implemented in emulsion[31] and suspension polymerization[32] and that hyperbranched polymers can be obtained with relatively high monomer to cross-linker ratios using conventional chain transfer agents.

In the present work we evaluate the potential of CCTP to synthesize hyperbranched polymers in emulsion polymerization. The efficiency of different CCTAs to inhibit cross-linking of the polymer particles is investigated as a function of the physiochemical properties of the cobalt(II) complexes used. A particular focus is the effect of CCTA partitioning on polymer architecture control. The results obtained with CCTP in emulsion polymerization are compared to previous experimental results reported on the synthesis of hyperbranched polymers using the "Strathclyde methodology" in homogeneous and heterogeneous polymerization systems. A general empirical correlation, that correlates the chain transfer activity to the divinyl monomer concentration is presented, which could benefit the further implementation of the "Strathclyde methodology" to synthesize functional hyperbranched polymers.

■ EXPERIMENTAL SECTION

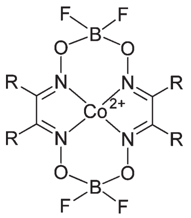
Materials. Methyl methacrylate (MMA, Aldrich, 99%) was passed over a column of basic aluminum oxide (Aldrich, ~150 mesh 58A) to remove the inhibitor and stored at 5 °C prior to polymerization. The cross-linker, ethylene glycol dimethacrylate (EGDMA, Aldrich, 98%), surfactant, sodium dodecyl sulfate (SDS, HP Biomedical, 99.8%), buffer, sodium hydrogen carbonate (Fisher, reagent grade), and the initiator, 2,2 azobis(2-methylpropionamide) dihydrochloride (V50, Aldrich, 97%) were used as received. For all experiments distilled, deionized water was used, purified by a Milipore Synergy ion exchange unit. The catalytic chain transfer agents, bis[(difluoroboryl) dimethylglyoximato]cobalt(II) (COBF), bis[(difluoroboryl) diethylglyoximato]cobalt(II) (COEtBF) and bis[(difluoroboryl) diphenylglyoximato]cobalt(II) (COPhBF) were prepared according to the method of Bakač and Espenson.[40] For all experiments, a single batch of catalyst was used. The intrinsic activities of the different catalysts were determined in MMA emulsion polymerization at 70 °C using a modified Mayo equation;[37] COBF (R = methyl): $C_T = 21 \times 10^3$; COEtBF (R = ethyl): $C_T = 22 \times 10^3$ and COPhBF (R = phenyl): $C_T = 6 \times 10^3$.

Strathclyde Emulsion Polymerizations. The polymerizations were performed in a 1 L glass reactor, equipped with a pitch blade impeller at 70 °C. In the case of COEtBF and COPhBF a catalyst stock solution was prepared by dissolving a carefully measured amount of catalytic chain transfer agent in MMA. In the case of COBF the total amount of catalyst required was dissolved in the total amount of monomer. An initiator solution was prepared by dissolving an accurate amount of V50 (0.50 g, 1.8×10^{-3} mol) in distilled deionized water (10 g). The total amount of monomer (MMA and EGDMA) was fixed at 93 g, corresponding to a phase ratio of $\beta = 0.25$ and a solids content of 19 wt %.

For a typical experiment (e.g., MMA:EGDMA = 98:2 mol % and 2.5 ppm COEtBF, entry H10 in Table 2), a catalyst solution was prepared by dissolving COEtBF (5.3 mg, 1.1×10^{-2} mmol) in deoxygenated MMA (50 mL). SDS (5.77 g, 2.0 × mol) and sodium carbonate (0.43 g, 4.0×10^{-3} mol) were weighed and dissolved in distilled deionized water (390 g) and subsequently added to the reactor. MMA (80.0 g, 0.80 mol) and EGDMA (3.6 g, 1.8×10^{-2} mol) were added to the reactor and the resulting emulsion was purged with nitrogen for 45 min. An aliquot of the catalyst stock solution (10 mL equaling 9.4 g MMA and 2.2×10^{-3} mmol COEtBF) was added and the emulsion was agitated for 15 min prior to the addition of the initiator solution (10 mL equaling 1.8×10^{-3} mol V50) to initiate the polymerization. The polymerization was continued for a maximum of 4 h after which cross-linking of the polymer particles was tested by dissolving the latex (5.0 g in 10 mL) and the precipitated polymer (30 mg in 1 mL) in THF.

Characterization. ^{1}H NMR spectroscopy was performed on a 400 MHz Bruker instrument in deuterated chloroform. The mol percentage of double bonds in the hyperbranched polymer structure was determined from the ratio of the integrals of the peaks of the vinyl protons at 5.3 and 6.0 ppm and the methoxy protons at 3.2 – 3.8 ppm. Linear size exclusion chromatography (LSEC) was performed using a Waters 2690 separation module and a model 410 differential refractometer. A set of five Waters Styragel HR columns (HR5.0, HR4.0, HR3.0, HR1.0, HR0.5) were used in series at 40 °C. Distilled tetrahydrofuran (THF) (Aldrich, 99%) was used as the eluent at a flow rate of 1 mL min^{-1}, and the system was calibrated using narrow molecular weight poly(styrene) standards ranging from 374 to 400 $\times 10^3$ g mol^{-1}. Mark–Houwink–Kuhn–Sakurada parameters were used for the polystyrene standards, $K = 1.14 \times 10^{-4}$ dL g^{-1}, $a = 0.716$, and for poly(methyl methacrylate), $K = 0.944 \times 10^{-4}$ dL g^{-1}, $a = 0.719$. Triple detection size exclusion chromatography (TDSEC) was performed using a Viscotek 270max separation module and a refractive index (RI), viscosity (IV) and light scattering (low angle LALS and right angle RALS) triple detector setup. A set of two porous PolyAnalytik columns with an exclusion limit molecular weight of 20×10^6 g mol^{-1} were used in series at 40 °C. Distilled THF was used as the eluent at a flow rate of 1 mL min^{-1}, and the system was calibrated using a narrow poly(styrene) standard of 99×10^3 g mol^{-1} with a refractive index of 0.185 mL g^{-1} and an intrinsic viscosity of 0.477 dL g^{-1}. The degree of branching of the hyperbranched polymers is determined using a random polydisperse(trifunctional) branching calculation and the linear polymers synthesized in the absence of EGDMA are used as the linear standards.

Scheme 1. General Structure of the Cobalt(II) Complexes Used for Molecular Weight and Polymer Architecture Control in Emulsion Polymerization[a]



[a] COBF: R = methyl; COEtBF: R = ethyl; and COPhBF: R = phenyl.

RESULTS AND DISCUSSION

CCTP in emulsion polymerization. The efficiency of catalytic chain transfer polymerization (CCTP) for the synthesis of hyperbranched polymers is evaluated in the emulsion copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). The catalytic chain transfer agents (CCTAs) bis[(difluoroboryl)methylglyoximato]cobalt(II) (COBF), bis[(difluoroboryl)ethylglyoximato]cobalt(II) (COEtBF), and bis[(difluoroboryl)phenyl glyoximato]cobalt(II) (COPhBF) (Scheme 1) were selected based on their different physiochemical properties, i.e. the difference in water-solubility. Different amounts of CCTA are added to the emulsion copolymerizations to allow for the synthesis of poly(MMA-co-EGDMA) polymers with different degrees of branching.

The cobalt(II) complexes used for CCTP are susceptible to partitioning in emulsion polymerization. This partitioning behavior is governed by the hydrophobicity of the substituent on the glyoxime ligand (see Scheme 1) and is quantified in terms of a partition coefficient ($m_{\mathrm{Co}} = [\mathrm{Co}]_{\mathrm{disp}}/[\mathrm{Co}]_{\mathrm{aq}}$, where $[\mathrm{Co}]_{\mathrm{disp}}$ and $[\mathrm{Co}]_{\mathrm{aq}}$ are the CCTA concentrations in the dispersed and aqueous phase, respectively). COBF (methyl substituent) is fairly water-soluble ($m_{\mathrm{Co}} = 0.72$),[37,41] whereas COPhBF (phenyl substituent) has no detectable water-solubility ($m_{\mathrm{Co}} = \infty$).[41] COEtBF (ethyl substituent) provides an intermediate case ($m_{\mathrm{Co}} = 19$).[42] The selected cobalt(II) complexes present cases where (i) the CCTA partitions predominantly to the aqueous phase (COBF), (ii) the CCTA partitions predominantly to the organic phase (COEtBF), and (iii) the CCTA partitions exclusively toward the organic phase (COPhBF). The spread in the m_{Co} of the different cobalt(II) complexes allows for an evaluation of the effect of partitioning of the control of the polymer architecture (i.e., cross-linked versus hyperbranched). This effect of partitioning of the chain transfer agent on the "Strathclyde methodology" has not been studied.

Prior to investigating the ability of CCTP to control the polymer architecture in emulsion polymerization, it is essential to establish whether the polymerizations are effectively controlled by CCTP. Efficient CCTP conditions result in a uniform distribution of the CCTA and as such ensures the production of polymer with a monomodal molecular weight distribution (MWD) of a predetermined molecular weight and a polydispersity index (D) of approximately 2.0.[33] While in a heterogeneous emulsion polymerization this is not necessarily the case,[43,44] the presence of the CCTA at the locus of polymerization (i.e., the polymer particles) is required to achieve proper molecular weight or polymer architecture control. As the majority of the cobalt(II) complexes display partitioning, a fraction of the CCTA is present in the aqueous phase and a discrepancy between the target and experimental molecular weight is observed.[37] Furthermore, the polymer particles typically outnumber the cobalt(II) molecules,[45] which makes efficient mass transport a prerequisite.

Table 1. Synthesis of Linear Poly(methyl methacrylate) in Emulsion Polymerization in the Presence of Different Catalytic Chain Transfer Agents[a]

	CCTA [-]	CCTA [ppm]	x^{b} [-]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	D [-]	DP_n (exp) [-]	DP_n (theo)^{c} [-]
L1	COBF	54	0.40	2468	4644	1.88	23	25
L2	COEtBF	2.5	0.81	3903	8636	2.21	43	63
L3	COEtBF	7.5	0.62	1221	2097	1.72	11	20
L4	COEtBF	10	0.55	1084	2604	2.40	13	15
L5	COPhBF	4.5	0.92	15617	36525	2.34	183	244
L6	COPhBF	8.0	0.71	7707	19895	2.58	100	131

[a] Experimental conditions: $V_M = 0.1$ dm^3, $\beta = 0.25$, $C_T(\mathrm{COBF}) = 21 \times 10^3$, $C_T(\mathrm{COEtBF}) = 22 \times 10^3$, $C_T(\mathrm{COPhBF}) = 6 \times 10^3$,[46] $m_{\mathrm{Co}}(\mathrm{COBF}) = 0.72$, $m_{\mathrm{Co}}(\mathrm{COEtBF}) = 19$, $m_{\mathrm{Co}}(\mathrm{COPhBF}) = \infty$. 1 ppm is defined as 1 mol of CCTA per 10^6 moles of monomer. All MWDs are determined using LSEC with a molecular weight range of 500 to 400 × 10^3 g mol^{-1}. [b] x is the fractional conversion. [c] DP_n (exp) is determined from the weight-average molecular weight (M_w): $DP_n = M_w/2M_0$.[47,48]

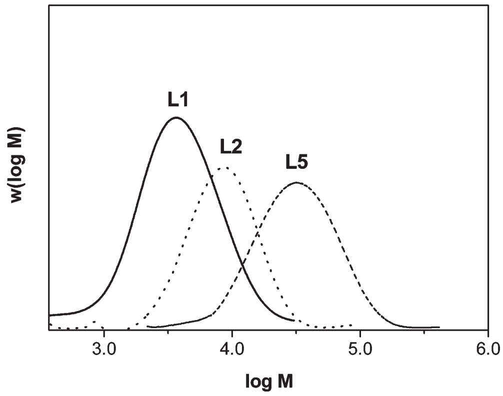


Figure 1. Molecular weight distributions of linear poly(methyl methacrylate) polymers synthesized using (L1) 54 ppm COBF, (L2) 2.5 ppm COEtBF, and (L5) 4.5 ppm COPhBF. The MWDs of L3, L4, and L6 are omitted for clarity reasons.

An analysis of the molecular weight distributions (MWD) for the COBF, COEtBF, and COPhBF-mediated emulsion polymerizations of MMA is presented in Table 1. Furthermore the experimentally obtained molecular weight distributions (MWDs) for polymerizations mediated with 54.0 ppm COBF (L1), 2.5 ppm COEtBF (L2), and 4.5 ppm COPhBF (L5), (which are illustrative for all of the entries collected in Table 1) are presented in Figure 1. It can be seen from Figure 1 and Table 1 that the MWDs in all cases are monomodal and that low molecular weight polymer with a D of approximately 2.0 has been synthesized. The number-average degree of polymerization (DP_n) for a CCTP-mediated emulsion polymerization can be calculated from eq 1[37]

$$DP_n = \frac{V_{\mathrm{disp}} C_{\mathrm{M,p}}}{C_T} \frac{1}{N_{\mathrm{Co},0}} \left(\frac{m_{\mathrm{Co}}\beta + 1}{m_{\mathrm{Co}}(\beta + 1)} \right) \left(1 + \frac{1}{\beta} \right) \tag{1}$$

where V_{disp} is the volume of the dispersed phase, $C_{\mathrm{M,p}}$ is the monomer concentration in the polymer particles (6.6 mol dm^{-3} for MMA),[49] C_T is the chain transfer constant, and β is the phase

Table 2. Analysis of the Polymer Architecture Control in the Catalytic Chain Transfer Mediated Emulsion Copolymerization of MMA and EGDMA

entry	CCTA [-]	CCTA [ppm]	$CCTA_p$[a] [ppm]	MMA [mol %]	EGDMA [mol %]	gel[b] [Y/N]	x[c] [-]
L1	COBF	54	8.2	100	0	N	0.40
H1		54	8.2	98	2	N	0.56
H2		54	8.2	96	4	N	0.36
H3		54	8.2	94	6	Y	0.57
H4		54	8.2	92	8	Y	0.43
L2	COEtBF	2.5	2.0	100	0	N	0.81
H5		2.5	2.0	99.75	0.25	N	0.91
H6		2.5	2.0	99.25	0.75	N	0.94
H7		2.5	2.0	99	1	N	0.89
H8		2.5	2.0	98	2	Y	0.83
H9		2.5	2.0	97	3	Y	0.80
L3	COEtBF	7.5	6.2	100	0	N	0.62
H10		7.5	6.2	98	2	N	0.51
H11		7.5	6.2	97	3	N	0.71
H12		7.5	6.2	96	4	Y	0.50
H13		7.5	6.2	95	5	Y	0.68
L4	COEtBF	10	8.3	100	0	N	0.55
H14		10	8.3	98	2	N	0.56
H15		10	8.3	96	4	N	0.45
H16		10	8.3	95	5	N	0.53
H17		10	8.3	94	6	Y	0.52
H18		10	8.3	92	8	Y	0.52
L5	COPhBF	4.5	4.5	100	0	N	0.96
H19		4.5	4.5	99.75	0.25	Y	0.67
H20		4.5	4.5	99.50	0.50	Y	0.66
H21		4.5	4.5	99	1	Y	0.94
L6	COPhBF	8.0	8.0	100	0	N	0.75
H22		8.0	8.0	99.75	0.25	Y	0.77
H23		8.0	8.0	99.50	0.50	Y	0.70
H24		8.0	8.0	99.25	0.75	Y	0.71

[a] The CCTA concentration at the locus of polymerization is determined via a mass balance using $V_{disp} = 0.1$ dm^3, $\beta = 0.25$, and m_{Co}(COBF) = 0.72, m_{Co}(COEtBF) = 19, and m_{Co}(COPhBF) = ∞. [b] Gel formation is determined by dissolving the latex (5 g latex in 10 mL of THF) and the dried polymer (30 mg in 1 mL of THF). [c] The conversion is determined after 4 h of polymerization.

ratio ($\beta = V_{disp}/V_{aq}$, where V_{aq} is the volume of the aqueous phase). For the polymerizations mediated with COBF, COEtBF, and COPhBF the theoretical DP_n can be calculated based on the amount of CCTA added to the polymerizations. Due to the differences in the partitioning behavior of the cobalt(II) complexes significantly more COBF is required to synthesize low molecular weight polymer when compared to e.g. COEtBF. It can be concluded from Table 1 that the theoretical values of DP_n are in good agreement with the experimentally obtained DP_n values. Therefore, it can be concluded that, despite the effects of CCTA partitioning, CCTP was effective since monomodal MWDs with a predetermined molecular weight and a D of approximately 2.0 are obtained.

Hyperbranched Polymers using CCTP in Emulsion Polymerization. COBF, COEtBF and COPhBF-mediated emulsion polymerization of MMA and EGDMA were performed to investigate the potential of CCTP to synthesize hyperbranched polymers, see Table 2. The emulsion copolymerizations are mediated with 54 ppm COBF, 2.5, 7.5, and 10 ppm COEtBF and 4.5 and 8.0 ppm COPhBF (1 ppm is defined as 1 mol of CCTA per 10^6 mol of MMA and EGDMA). At these CCTA concentrations relatively low molecular weight polymer is synthesized (see Table 1). These predetermined levels of CCTA were chosen to cover a range of chain transfer activities, as will be illustrated in detail in the next section. Briefly, targeting a range of molecular weights allows for the incorporation of a broader range of EGDMA which allows for an enhanced accuracy when determining the cross-linking threshold (see the next section).

The synthesized poly(MMA-co-EGDMA) latexes were all colloidally stable with the exception of the COBF-mediated emulsion copolymerizations. These latexes (L1,H1−H4) displayed phase separation after quenching of the polymerization. It can be seen from Table 2 that the final conversion reached after 4 h of polymerization, roughly, equals 45%. COBF displays a strong partitioning behavior in emulsion polymerization and as a consequence severely affects the aqueous phase polymerization kinetics. As a result the rate of polymerization is low and the colloidal stability of the formed latex affected.[46] CCTA partitioning is of less significance in COEtBF and COPhBF-mediated emulsion polymerizations which results in higher rates of polymerization and a good colloidal stability of the latex.[46] Consequently, it can be concluded that the use of COEtBF or COPhBF is preferred for polymer architecture control with respect to the

Table 3. Molecular Weight Analysis of the Hyperbranched pMMA-co-pEGDMA Polymers Synthesized Using 54 ppm COBF and 2.5 ppm COEtBF

entry	CCTA [-]	EGDMA [mol %]	C=CH$_2$[a] [mol %]	M_n[b] [g mol^{-1}]	M_w[b] [g mol^{-1}]	$Đ$ [-]	branching number[c]	g′ [c]
L1	COBF	0.0	3.0	2468	4644	1.88	0.000	1.000
H1		2.0	3.0	5087	16240	3.19	0.168	0.601
H2		4.0	7.2	6739	22563	3.35	10.21	0.263
L2	COEtBF	0.0	2.8	3903	8636	2.21	0.000	1.000
H5		0.25	2.3	3271	10623	3.25	8.176	0.537
H6		0.75	2.4	3381	16938	5.01	20.99	0.110
H7		1.0	2.6	2815	29976	10.7	60.39	0.042

[a] Determined from ^{1}H NMR analysis. [b] MWD analysis of the linear polymers (L1 and L2) performed on LSEC using a RI detector. MWD analysis of the hyperbranched polymers (H1, H2, and H5−H7) performed on a TDSEC using triple detector analysis. [c] The Zimm branching factor is calculated from the OmniSEC software.

colloidal stability of the latex. In particular when low molecular weight polymer is targeted (and high amounts of COBF are required) as is the case here.

The MMA/EGDMA molar ratio was varied systematically until complete cross-linking of the polymer particles occurred, see Table 2. The differentiation between hyperbranched and cross-linked polymer particles is based on the dissolution of the final latex and precipitated polymer in tetrahydrofuran (THF). Hyperbranched poly(MMA-co-EGDMA) polymers are completely soluble in THF, whereas their cross-linked counterparts are not. It can be concluded from the results presented in Table 2 that hyperbranched polymers can be successfully synthesized in emulsion polymerization using CCTP. The maximum EGDMA content that yielded hyperbranched polymers proved to be 4.0 mol % for 54 ppm COBF and 10 ppm COEtBF. When the amount of COEtBF was lowered to 7.5 and 2.5 ppm, the maximum EGDMA content was reduced to 3.0 and 1.0 mol %, respectively. Surprisingly, no hyperbranched poly(MMA-co-EGDMA) polymers could be obtained for the COPhBF-mediated emulsion copolymerizations. Furthermore, it can be seen from Table 2 that the maximum MMA/EGDMA molar ratio that yields hyperbranched polymers scales to the amount of CCTA added. This result is in line with earlier observations made by Camerlynck et al., where an increase in the maximum EGDMA content to obtain hyperbranched polymers from 4.0 to 10.0 mol % was observed as the CCTA (= COPhBF) was increased from 8.0 to 24 ppm, respectively.[24]

It can be seen from Table 2 that a maximum EGDMA content of 4.0 mol % is found for both 54 ppm COBF and 10 ppm COEtBF. Both CCTAs partition toward the aqueous phase, however, to different extents. When corrected for the effect of partitioning, the amount of CCTA at the locus of polymerization in both polymerizations equals approximately 8.2 ppm. Both sets of polymerizations are thus mediated by a comparable CCTA concentration and as the intrinsic activities of these complexes are very similar, it appears logical that the maximum EGDMA content prior to cross-linking is very similar as well.

For the emulsion polymerizations mediated with 4.5 and 8.0 ppm COPhBF, the EGDMA content was increased from 0 to 3.0 mol %. However, no hyperbranched polymers could be synthesized within this MMA/EGDMA molar ratio range, see Table 2. The discrepancy between COPhBF and the other CCTAs is the difference in partitioning behavior and the mode of mass transport of these cobalt(II) complexes.[50] COBF and COEtBF possess some water-solubility that results in partitioning, but also allows for fast mass transport of these cobalt(II) complexes. No mass transport limitations exist for these CCTAs and in terms of molecular weight or polymer architecture control and, consequently, the dispersed phase (i.e., monomer swollen micelles, monomer droplets, and polymer particles) can be regarded as one continuous phase. COPhBF possesses no detectable water-solubility, and as a result no mass transport of COPhBF via the aqueous phase can occur. Mass transport of COPhBF is thought to occur between collisions between monomer swollen micelles, monomer droplets, and polymer particles.[50] This mass transport mechanism possesses some mass transport limitations for COPhBF between monomer droplets and polymer particles. In the early stages of the polymerization (up to the end of interval II which marks the disappearance of the monomer droplets) a fraction of the amount of COPhBF is exclusively located in the monomer droplets and not active in molecular weight or polymer architecture control. Consequently, the concentration of COPhBF at the locus of polymerization is continuously changing in the initial stages of the polymerization, altering the predetermined MMA/EGDMA molar ratio. Initially, the probability of cross-linking is relatively high as only a small amount of COPhBF is available for polymer architecture control. As the monomer droplets shrink (interval II) and eventually disappear (interval III), the MMA/EGDMA molar ratio will be continuously increasing, thereby increasing the likelihood of branching. The resulting polymer from these polymerizations likely is partially cross-linked and partially hyperbranched.

Hyperbranched polymers synthesized using 54 ppm COBF (H1 and H2) and 2.5 ppm COEtBF (H5−H7) were analyzed by ^{1}H NMR spectroscopy and triple detector size exclusion chromatography (TDSEC), see Table 3. The polymerizations mediated with 7.5 and 10 ppm COEtBF resulted in a very low molecular weight polymer that could not be analyzed accurately on the available TDSEC. The polymerizations mediated with 4.5 and 8.0 ppm COPhBF yielded cross-linked networks and no further analysis could be performed. It can be seen from Table 3 that the mol fraction of vinyl unsaturations increases in the poly(MMA-co-EGDMA) structure as the EGDMA content increases. Pendant vinyl unsaturations are present due to partially reacted EGDMA fragments in the polymer backbone and due to the chain transfer reaction of the CCTA. However, as in each series the amount of CCTA is constant, the increasing mol fraction of vinyl unsaturations originates from an increasing amount of partially reacted EGDMA molecules. This effect is particularly evident for the polymerization mediated with 54 ppm COBF and 4 mol % EGDMA (H2), see Table 3.

The MWDs of the hyperbranched polymers synthesized in the presence of 54 ppm COBF and 2.5 ppm COPEtBF measured

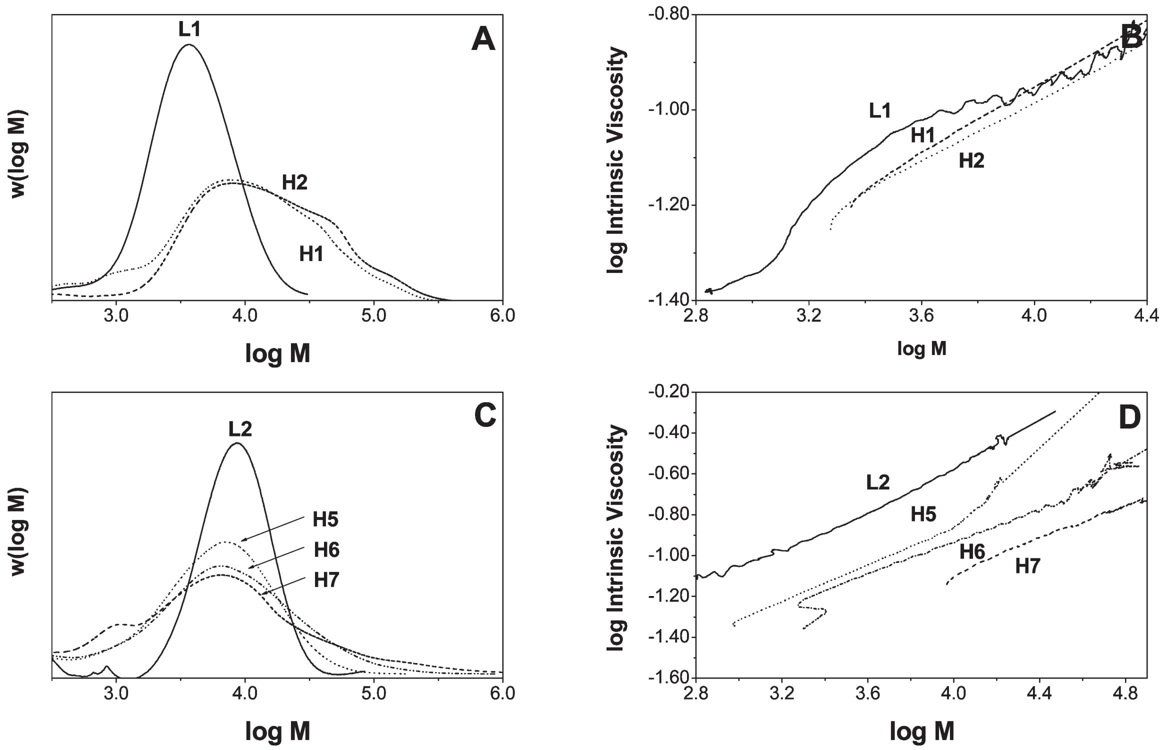


Figure 2. Molecular weight distributions (A and C) and the intrinsic viscosity (B and D) of the hyperbranched p(MMA-co-EGDMA) polymers in the presence of 54 ppm COBF (A and B) and 2.5 ppm COEtBF (C and D).

using TDSEC are presented in Figure 2, panels A and C, respectively. It can be seen from Figure 2, panels A and B that, compared to the linear polymers L1 and L2, broad MWDs are obtained upon the copolymerization of EGDMA. Furthermore, it can be seen that the MWD broadens (quantified by the *D* as reported in Table 3) as the mol fraction of EGDMA increases, an indication of the formation of hyperbranched polymers.

The level of branching of the poly(MMA-co-EGDMA) polymers can be determined from the average Zimm branching factor (g'),[51] which represents the ratio of the squared gyration radii of branched and linear polymers of similar molecular weights. The g' of a linear polymer by definition equals 1, whereas for a branched polymer the value of $g' < 1$. This originates from the fact that the radius of gyration of a hyperbranched polymer is smaller than that of a linear polymer of comparable molecular weight. The TDSEC provides a triple detector array, including differential refractometry (RI), viscometry (VI) and light scattering (LS). Coupling of the VI and LS detectors allows for the determination of branching which is calculated from the Zimm−Stockmayer equations. The MWDs of the hyperbranched polymers presented in Figure 2, panels A and C, were analyzed and compared to their linear analogues, i.e. the linear polymers formed in the homopolymerization of MMA in the presence of 54 ppm COBF (L1) or 2.5 ppm COEtBF (L2).

It can be seen from Figure 2, panels B and D, that the intrinsic viscosity of the hyperbranched polymers is indeed lower than their linear counterparts. The analysis of the hyperbranched polymers is presented in Table 3. When compared to the linear polymers synthesized in the absence of EGDMA the number of branched increases while the average Zimm branching factor decreases. These results are a clear indication that the synthesized polymers are increasingly branched as the molar ratio of EGDMA is increased.

Predicting the Molecular Architecture. Hyperbranched polymers as dendrimer analogues are finding increasing use as smart materials for biological, medical and engineering applications.[2−8] Therefore, it would be advantageous to predict the polymer architecture (i.e., cross-linked versus hyperbranched) based on process parameters such as the concentration of cross-linker and type and concentration of chain transfer agent in the polymerization process. Branching of the polymer is typically achieved by balancing the concentration of cross-linker and chain transfer agent (CTA). Although this optimization strategy works for a specific combination of monomers and chain transfer agent, it fails when different monomers or chain transfer agents are required. Chain transfer constants of chain transfer agents can differ by orders of magnitude depending on the chain transfer agent (e.g., $C_T \approx 1-10$ for a thiol and $C_T \approx 10^4$ for a CCTA) as well as on the monomer (e.g., for COBF $C_T \approx 40 \times 10^4$ for MMA and $C_T \approx 8 \times 10^3$ for styrene).[33] Such significant differences in the C_T will affect the maximum concentration of divinyl monomer that can be copolymerized in the presence of a given chain transfer agent. Therefore, it is advantageous to balance the concentration of divinyl monomer to the chain transfer activity, which can be expressed in terms of the chain transfer frequency (f_{tr}).[46] Equation 2 correlates the chain transfer frequency to the rate constant of chain transfer (k_{tr}) and the concentration of chain transfer agent ([T]). Expressing the chain transfer activity in terms of the chain transfer frequency eliminates potential differences between chain transfer agents, in terms of their concentration and their intrinsic activity.

$$f_{tr} = k_{tr}[T] \qquad (2)$$

Another distinct advantage of using the chain transfer frequency is that homogeneous and heterogeneous polymerization systems can be compared directly. Defining [T] as the chain

Table 4. Determination of the Chain Transfer Constant (C_T) and the Rate Coefficient of Chain Transfer (k_{tr}) from the Experimental Molecular Weight Results for MMA Polymerizations in the Absence of a Divinyl Monomer[a]

ref	CTA [-]	$[T]$ [mol dm^{-3}]	M_w [g mol^{-1}]	D [-]	DP_n [-]	C_T^{app} [-]	k_{tr}^{app} [dm^3 mol^{-1} s^{-1}]	f_{tr} [s^{-1}]
24	COPhBF	1.2×10^{-5}	13500	N/A	68	1852	2.7×10^6	262
	COPhBF	2.4×10^{-5}	10500	N/A	53	1190	1.7×10^6	525
	COPhBF	3.6×10^{-5}	4000	N/A	20	2083	3.0×10^6	787
31	BT	0.19	12000	1.88	60	0.83	0.78×10^4	146
32	DDT	0.02	85000	1.70	425	1.07	0.14×10^4	29.0
	DDT	0.05	41300	1.75	207	0.97	0.13×10^4	59.6
	DDT	0.07	31900	1.67	160	0.89	0.12×10^4	77.2
	DDT	0.08	27700	1.75	139	0.90	0.12×10^4	88.9
	DDT	0.08	14300	1.79	128	0.87	0.11×10^4	96.2
	DDT	0.19	6200	1.95	61	0.83	0.11×10^4	203
16	DDT	0.07	23900	1.98	120	0.83	0.11×10^4	77.3
	DDT	0.07	18500	1.65	112	0.89	0.12×10^4	83.5

[a] The average k_{tr} values used for the calculation of f_{tr} equal 2.5×10^7 dm^3 mol^{-1} s^{-1} for ref 24, 7.8×10^2 dm^3 mol^{-1} s^{-1} for ref 31, 1.2×10^3 dm^3 mol^{-1} s^{-1} for ref 32, and 1.1×10^3 for ref 16. For ref 20, the value of k_{tr} ranges from 1.5×10^3 to 2.5×10^3 dm^3 mol^{-1} s^{-1} depending on the mol fraction of DVB added to the polymerization.

transfer agent concentration at the locus of polymerization eliminates the effects of chain transfer agent partitioning. Consequently, the chain transfer frequency allows for a direct comparison of different "Strathclyde methodology" polymerization systems. This principle has been used prior to directly compare different CCTAs that display different partitioning behavior in emulsion polymerization.[46]

The chain transfer frequency of a CTA-mediated polymerization can be calculated in two ways: (*i*) f_{tr} can be estimated directly from the k_{tr} value and the CTA concentration or (*ii*) f_{tr} is estimated from the DP_n of a polymerization in the absence of the divinyl monomer. Estimating f_{tr} from the DP_n (route *ii*) is advantageous if the activity of the CTA in combination with the investigated monomer(s) is not reported or if the partitioning behavior of the CTA is unknown. In this case, the Mayo equation can be used to estimate the apparent chain transfer constant (C_T^{app}) and, subsequently, the apparent chain transfer rate coefficient (k_{tr}^{app}); see eq 3.

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_T^{app}\frac{[T]}{[M]} = \frac{1}{DP_{n,0}} + \frac{k_{tr}^{app}}{k_p}\frac{[T]}{[M]} \qquad (3)$$

The method based on DP_n is often applicable; however, it is less suitable when the radical center of the vinyl monomer differs from the divinyl monomer. For example, if MMA is copolymerized with divinylbenzene (DVB), there is a significant difference between the k_{tr} value for, e.g., 1-DDT and MMA (methacrylic radial) and 1-DDT and DVB (styril radical). At 70 °C the C_T for 1-DDT and MMA and styrene are 0.55 and 19, respectively.[52] If the DP_n of a MMA homopolymerization is used to determine k_{tr}^{app}, the chain transfer activity in the copolymerization of MMA and DVB could be underestimated, depending on the mol fraction DVB used. In this case a better estimate for f_{tr} can be obtained from an averaged k_{tr} value and the CTA concentration. The average k_{tr} ($\langle k_{tr}\rangle$) in a chain transfer copolymerization of monomers A and B can be expressed in terms of the mol fractions of radicals $\sim$A• and $\sim$B• (ϕ_A and ϕ_B, respectively) and the k_{tr} of these radicals to the CTA ($k_{tr,A}$ and $k_{tr,B}$, respectively), see eq 4.[47,53]

$$\langle k_{tr}\rangle = \phi_A k_{tr,A} + (1 - \phi_A)k_{tr,B} \qquad (4)$$

As for the copolymerizations reported here (MMA/EGDMA, identical radical center) and MMA/DVB (copolymerization ratios for MMA and DVB $\sim$ 0.46 and $\sim$0.52, respectively)[52] no large composition drift is expected. Consequently, the mol fractions of radicals A and B can be replaced by the mol fractions of both monomers in the feed composition. This allows for a straightforward estimation of k_{tr} as a function of the monomer feed composition.

Sherrington and co-workers have provided a substantial body of research on the fundamentals of the "Strathclyde methodology" for copolymerizations of MMA with different divinyl monomers in the presence of different CTAs in homogeneous and heterogeneous systems. Results reported by Camerlynck[24] et al. and O'Brien[16] et al. are obtained in homogeneous solution polymerization of MMA. O'Brien et al. used but-2-ene-1,4-diacrylate (BDA) in the presence of 1-DDT. As the chain transfer activity of 1-DDT to an acrylate is not known, it was decided to estimate f_{tr} from the DP_n reported by O'Brien for a MMA homopolymerization. Camerlynck et al.[24] copolymerized MMA with EGDMA in the presence of COPhBF. The radical activities of MMA and EGDMA with respect to COPhBF are likely very similar and therefore f_{tr} is estimated from the DP_n of the reported MMA homopolymerizations. For the solution polymerizations mediated with COPhBF[24] and 1-dodecanethiol (DDT),[16] average C_T^{app} values of 1.7×10^3 and 0.86 are calculated, respectively; see Table 4. These values of C_T^{app} were used to calculate f_{tr} throughout all the reported copolymerizations. Isaure et al.[20] reported the solution copolymerization of MMA with DVB mediated by 1-DDT. In this specific case the f_{tr} was calculated for each individual experiment based on an average k_{tr} estimated from the mol fractions of MMA and DVB in the copolymerization. The k_{tr} values used for DDT are 0.72×10^3 and 24.9×10^3 for MMA and DVB, respectively.

Results reported by Baudry et al.[31] and Chisholm et al.[32] are reported in heterogeneous emulsion and suspension polymerization. Baudry et al.[31] copolymerized MMA and DVB in the presence of benzylthiol (BT). Chisholm et al.[32] copolymerized MMA and ethylene glycol diacrylate (EGDA) in the presence of 1-DDT. As the k_{tr} values of MMA and styrene to BT and EGDA to 1-DDT to the best of our knowledge are not reported, it was opted to estimate k_{tr} and f_{tr} from eq 3. It can be seen from Table 3 that for BT and 1-DDT values of 0.83 and 0.92 are calculated, respectively. It is interesting to note that the values for 1-DDT in solution and suspension appear very similar. As 1-DDT has an extremely low water solubility[54] partitioning likely is not an issue and this is reflected in the very similar C_T^{app} values in solution and suspension polymerization. A summary of the C_T^{app}, k_{tr} and f_{tr} values determined for the literature data are collected in Table 4 and used to construct Figure 3.

Figure 3 presents the chain transfer activity (f_{tr}) as a function of the divinyl monomer mol fraction as calculated from the experimental results reported in references.[16,20,24,31,32] Note that for the calculation of f_{tr} for the results reported by Camerlynck et al.[24] a C_T^{app} value of 17 × 10^3 is used, which is in better agreement with reported values for COPhBF. The value calculated from the experimental data ($C_T^{app} = 1.7 \times 10^3$ in solution polymerization) is rather low as these cobalt complexes typically display activities ranging from (18−24) × 10^3.[33] Hyperbranched and cross-linked polymers are indicated with open and closed symbols, respectively. It can be seen from Figure 3 that, for a given f_{tr}, a maximum monomer/divinyl monomer mol fraction exists that allows for the synthesis of hyperbranched polymers. Moreover, the correlation between the chain transfer frequency and the maximum monomer/cross-linker molar ratio appears to be linear (see the dotted line in Figure 3). Based on these results presented in Figure 3, it can be estimated that the ratio (α) of the chain transfer frequency in s^{-1} and the mol fraction of divinyl monomer (φ_x) in mol % should be above 85 to synthesize hyperbranched polymers in MMA copolymerizations, see eq 5. In other words, the chain transfer frequency should be sufficiently high to prevent macro-gelation.

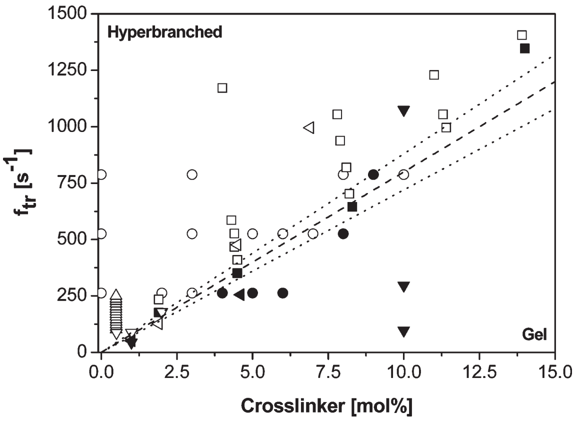


Figure 3. Empirical fit of the available literature data on the Strathclyde methodology. Solid symbols indicate cross-linked polymer, and open symbols indicate hyperbranched polymer. The dashed line indicates α = 85, the dotted lines indicate a 10% confidence interval. (○) Camerlynck et al.[24] MMA-EGDMA using COBF in solution polymerization, (□) Baudry et al.[31] MMA-DVB using benzylthiol in emulsion polymerization, (△) Chisholm et al.[32] MMA-EGDA using 1-dodocylthiol in suspension polymerization, (▽) O'Brien et al.[16] MMA-BDA using 1-dodecylthiol in solution polymerization and (left pointing triangle) Isaure et al.[20] MMA-DVB using 1-dodecylthiol in solution polymerization. Note that for the Camerlynck data a more representative C_T value of 17 × 10^3 has been used (see text for further details).

$$\alpha = \frac{f_{tr}}{\varphi_X} > 85 \qquad (5)$$

The results in Figure 3 show that polymer architecture control using the "Strathclyde methodology" can be reduced to the copolymerization feed composition and the chain transfer frequency. Moreover, this empirical correlation accounts for differences in the intrinsic activity of the CTAs. However, it should be noted that for this empirical correlation only copolymerizations of MMA with divinyl monomers have been considered.

The experimental results obtained with CCTP in the emulsion copolymerizations of MMA and EGDMA as described in the previous section can be used to further validate the empirical correlation derived above from available literature. COBF and COEtBF partition in dispersed phase polymerizations, whereas COPhBF, BT and 1-DDT do not. Validation of the empirical correlation with CCTP in emulsion polymerization, therefore, can demonstrate if the effects of partitioning are effectively captured.

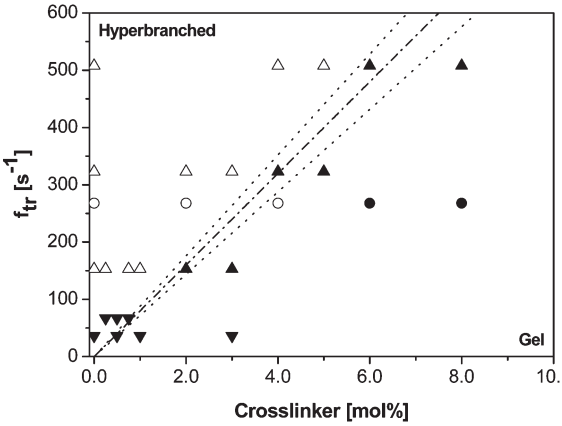


Figure 4. Successful validation of the empirical correlation (eq 5) with experiments reported in this work with MMA and EGDMA using COBF, COEtBF, and COPhBF in emulsion polymerization. Solid symbols indicate cross-linked polymer, and open symbols indicate hyperbranched polymer. The dashed line indicates α = 85, and the dotted lines indicate a 10% confidence interval. (○) 54.0 ppm COBF; (△) 10.0, 7.5, and 2.5 ppm COEtBF; and (▽) 4.5 and 8.0 ppm COPhBF.

Table 5. Determination of the Chain Transfer Constant (C_T) and the Rate Coefficient of Chain Transfer (k_{tr}) from the Experimental Molecular Weight Results in the Absence of a Cross-Linker

entry	$[CCTA]_0$[a] [mol dm^{-3}]	$[CCTA]_p$[b] [mol dm^{-3}]	M_w [g mol^{-1}]	D [-]	DP_n[c] [-]	10^{-3}	k_{tr}^{app} [dm^3 mol^{-1} s^{-1}]	f_{tr} [s^{-1}]
L1	9.8×10^{-5}	7.4×10^{-5}	4644	1.88	25	2.6	0.3×10^7	268
L2	4.5×10^{-6}	1.9×10^{-5}	8636	2.21	43	32.4	3.4×10^7	153
L3	1.4×10^{-5}	5.8×10^{-5}	4097	1.84	21	22.1	2.3×10^7	323
L4	1.9×10^{-5}	7.7×10^{-5}	2604	2.40	13	26.0	2.7×10^7	508
L5	1.5×10^{-5}	7.4×10^{-5}	19895	2.58	100	4.3	3.4×10^7	67
L6	6.5×10^{-6}	3.3×10^{-5}	36525	2.34	183	4.3	3.4×10^7	36

[a] $[CCTA]_0$ is the CCTA concentration per volume of emulsion ($=V_{aq} + V_{disp}$). [b] $[CCTA]_p$ is the CCTA concentration in the dispersed phase. [c] DP_n is determined from the weight-average molecular weight (M_w): $DP_n = M_w/2M_0$.[47,48]

For the CCTP copolymerizations of MMA and EGDMA, f_{tr} is estimated from the DP_n of the MMA homopolymerizations L1−L6 collected in Table 2. The cobalt(II) complexes used partition in emulsion polymerization and, consequently, the C_T^{app} values calculated from the experimentally obtained DP_n encompass the effects of partitioning.[36] The chain transfer frequency is subsequently calculated using the macroscopic CCTA concentration (moles of CCTA per unit volume of emulsion). Note that for the calculation of f_{tr} for the CCTAs that display partitioning in emulsion polymerization the CCTA concentration at the locus of polymerization also could have been used. In this scenario C_T^{app} should be calculated based on the CCTA concentration at the locus of polymerization, accounting for the effects of partitioning. The two methods are identical; however, if the partitioning behavior of a CTA is unknown, the method based on DP_n may be preferred. The values for C_T^{app}, k_{tr}^{app}, and f_{tr} for COBF, COEtBF, and COPhBF in emulsion homopolymerizations of MMA are collected in Table 5.

It can be seen from Table 5 that the values of C_T^{app} differ greatly between the different CCTAs but are fairly consistent for each individual CCTA. Experimentally determined C_T values in bulk polymerization range between 24×10^3 to 40×10^3 for COBF and COEtBF and between 18×10^3 and 24×10^3 for COPhBF.[33] For the COBF-mediated polymerization, a C_T^{app} value of 2.6×10^3 is calculated, 1 order of magnitude lower than expected based on the bulk value. A substantial fraction of COBF partitions toward the aqueous phase, which explains the lower observed chain transfer activity. COEtBF only marginally partitions toward the aqueous phase and consequently the COEtBF-mediated emulsion polymerizations display C_T^{app} values close to the bulk value. The C_T^{app} values for COPhBF are very similar to the value for the complex as measured in bulk polymerization ($C_T \approx 6 \times 10^3$ for the specific batch used). The chain transfer frequencies in the CCTP emulsion polymerizations range from approximately 40 to 500 s^{-1} which was selected to allow for the incorporation of significant amounts of EGDMA and to cover a significant range in f_{tr}.

Figure 4 presents a comparison between the empirical correlation and the results reported on architecture control using CCTP in emulsion polymerization. Open symbols indicate hyperbranched polymer architectures, whereas closed symbols indicate gelation of the polymer particles. It can be seen from Figure 4 that a good agreement between the experimental results and empirical correlation is obtained. These results illustrate that the empirical correlation (eq 5) not only accounts for different CTAs but also successfully encompasses the effects of partitioning of the CTA. This makes the empirical correlation and effective tool to predict the polymer architecture in MMA homogeneous and heterogeneous copolymerizations with a range of divinyl monomers and in the presence of different CTAs.

CONCLUSIONS

The results of this work clearly show that successful architecture control can be achieved in emulsion polymerization using catalytic chain transfer polymerization as the chain transfer chemistry. Hyperbranched polymers were obtained with both COBF and COEtBF, however, COEtBF likely is a more suitable choice largely due to the reduced effect on the course of the polymerization and colloidal stability of the polymer latex. With COPhBF, under the investigated conditions, no effective control over the polymer architecture could be obtained due to mass transfer limitations that exist for this cobalt(II) complex within a heterogeneous emulsion polymerization system.

An empirical correlation was derived and compared to experimental data reported here as well as on the "Strathclyde methodology" available in literature. The chain transfer frequency was used as an independent variable to be able to account for differences between in the activity and partitioning behavior of chain transfer agents. The chain transfer frequency can be correlated to the mol fraction of divinyl monomer to predict the polymer architecture. It was concluded that the ratio of the chain transfer frequency (s^{-1}) and the cross-linker concentration (mol %) should exceed 85 to synthesize hyperbranched polymers in MMA copolymerizations. If, for a set amount of chain transfer agent, the ratio of the chain transfer frequency and the mol fraction of divinyl monomer is decreased toward 85, the degree of branching increases as indicated by an increasing D and decreasing g' of the MWD. The empirical correlation was further validated using the experimental results obtained using CCTP in emulsion polymerization and were found to be in good agreement.

The empirical correlation presented here provides a useful tool for polymer scientists to readily predict the polymer architecture (i.e., cross-linked or hyperbranched) for free radical copolymerization of MMA and divinyl monomers in the presence of chain transfer agents.

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