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Binary Copolymerization with Catalytic Chain Transfer. A Method for Synthesizing Macromonomers Based on Monosubstituted Monomers

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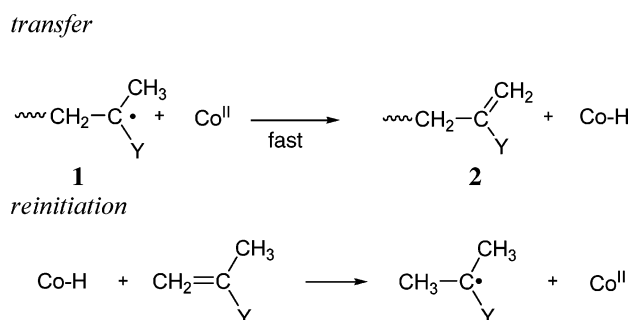
ABSTRACT: With appropriate choice of conditions, copolymerization of monosubstituted monomers [$\text{CH}_2=\text{CHX}$: e.g., styrene, butyl acrylate (BA)] in the presence of small amounts of an α -methylvinyl monomer [$\text{CH}_2=\text{C}(\text{CH}_3)\text{Y}$: e.g., α -methylstyrene (AMS), methyl methacrylate (MMA), methacrylonitrile (MAN)] and a cobaloxime as chain transfer catalyst provides a route to macromonomers that are composed largely of the monosubstituted monomer and yet have a chain end derived from the α -methylvinyl monomer ($-\text{CH}_2-\text{C}(\text{CH}_3)=\text{Y}$). The various factors (temperature, concentrations, type of cobaloxime, types of monomer) that influence molecular weight and end group purity and the importance of the various side reactions that may complicate the process are described. Macromonomer purity is enhanced by increasing the concentration of the α -methylvinyl monomer and reducing the cobaloxime concentration. It also depends on the structure of the cobaloxime, increasing in the series where the ligands are derived from dimethyl glyoxime < diethyl glyoxime ~ diphenyl glyoxime, and the α -methylvinyl monomer, increasing in the series where Y is CO_2R < CN < Ph . For styrene–AMS copolymerization, macromonomer purity (the fraction of AMS-derived ends) was enhanced by increasing the reaction temperature. For BA–AMS copolymerization, macromonomer purity was enhanced by decreasing the reaction temperature. However, it is necessary to use a high reaction temperature to limit the extent of macromonomer copolymerization that occurs as a side reaction at high monomer conversion. High purity, AMS terminal BA macromonomers can be prepared by BA–AMS copolymerization at 125 °C with as little as 2 mol % AMS. We also show how the overall composition, molecular weight, and end group functionality of copolymers formed in the presence of a chain transfer agent can be predicted using classical statistics and point out some problems with previous treatments. Analytical expressions which describe zero conversion binary copolymerization in the presence of a transfer agent are derived and successfully applied to the above-mentioned system. The effective transfer constants of cobaloxime transfer catalysts are reported. Those observed in copolymerizations of vinyl and α -methylvinyl monomers are reduced with respect to values observed in homopolymerization of α -methylvinyl monomers because of reversible consumption of the cobalt complex as an adduct to the vinyl monomer. Transfer constants of macromonomers with AMS end groups in styrene polymerization at 120 °C are in the range 0.11–0.15. At lower temperatures (80 °C), macromonomer copolymerization dominates over chain transfer and the effective transfer constant is ~ 0 .

Introduction

Macromonomers with end group structure **2** have utility as chain transfer agents^{1–7} and as precursors to block,^{8–10} graft,^{1,2,10–18} and end-functional polymers.^{19–21} Polymerizations of methacrylate esters [e.g. methyl methacrylate (MMA); Y = CO_2Me] and some other monomers with an α -methyl group in the presence of cobaloximes as chain transfer catalysts can provide such macromonomers in high yield. The generally accepted mechanism for chain transfer is shown in Scheme 1 and the overall process may be viewed as a catalyzed chain transfer to monomer.²² The cobaloxime may then either be called a “chain transfer catalyst”²² or a “catalytic chain transfer agent”.²³ The process of catalytic chain transfer has been the subject of a number of recent reviews.^{3,24–26}

Polymerizations of monosubstituted monomers [e.g. styrene, butyl acrylate (BA), methyl acrylate (MA)] in the presence of cobaloximes as chain transfer catalysts provides polymer chains possessing an internal (1,2-disubstituted) double bond as an end group structure (i.e., **5**, Scheme 2). These double bonds have a low reactivity in polymerization and consequently the polymers have little utility with respect to the above-

Scheme 1



mentioned applications. A side reaction, involving reversible coupling of the propagating radical (**3**) with the cobalt(II) catalyst, to give a relatively stable alkylcobalt(III) species (**4**), further complicates the polymerizations (Scheme 2). Probably as a consequence of this side reaction, inhibition, retardation and/or loss of catalyst activity are often reported.^{22,27,28}

A mechanism for the transfer step in copolymerization of a monosubstituted monomer (S) with an α -methylvinyl monomer (A) in the presence of a chain transfer catalyst is shown in Scheme 3. Provided there is specificity for reaction between the chain transfer catalyst and the propagating radical (**1**) which has a

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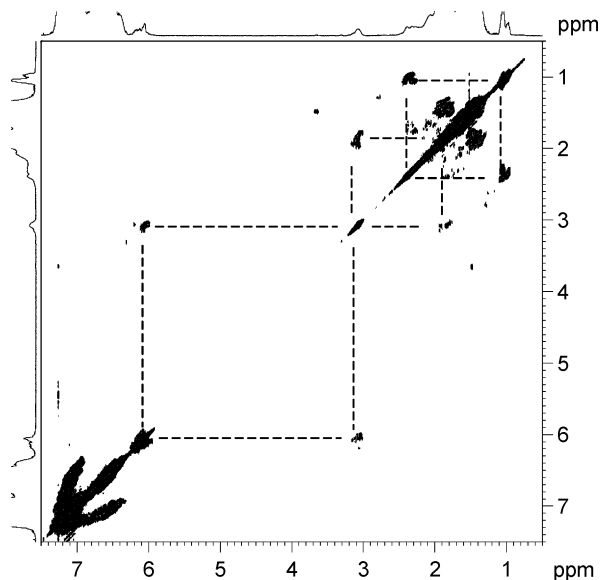


Figure 1. COSY spectrum of polystyrene (**14**, \bar{M}_n 1630) showing connectivities between the end group and adjacent hydrogens. The spectrum was obtained at 298 K in CDCl_3 using a Bruker DRX 500 spectrometer at (see text for further experimental details).

(CDCl_3). Chemical shifts are reported in ppm from TMS rounded to the nearest 0.05 ppm and coupling constants are quoted to the nearest 0.5 Hz. The COSY experiment (Figure 1) used a standard Bruker library sequence (cosygpqf45) with the following parameters: 4096 FID data points, 6510 Hz sweep width, 0.31 s acquisition time, 1.0 s relaxation delay, and 512 experiments, multiplied by an unshifted sine function in both dimensions and Fourier transformed over 2048×1024 points. Number-average degrees of polymerization (DP), number-average molecular weights (\bar{M}_n) and dispersities (the ratio of the weight-average and the number-average molecular weights— \bar{M}_w/\bar{M}_n) were determined by gel permeation chromatography (GPC) performed on a Waters Associates liquid chromatograph equipped with differential refractometer and a set of Waters UltraStyragel columns (300 mm \times 7.5 mm, 5 μm particle size, and 10^6 , 10^5 , 10^4 , 10^3 , 500 and 100 Å pore size). The column set gave an approximately linear calibration for the molecular weight range 200 to 1×10^7 g mol^{-1} that was fitted to a third-order polynomial. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent at 22 ± 1 °C. The columns were calibrated with narrow polydispersity polystyrene standards. High performance liquid chromatography (HPLC) was performed with a Hewlett-Packard 1090 HPLC system equipped with a diode array detector and a Beckman Ultrasphere ODS column (250 mm \times 10 mm) with 60:40 water:methanol (flow rate of 3 mL/min) as eluent at 30 °C. Conversions were determined gravimetrically by determining the mass of the residue after exhaustive evaporation of monomer.

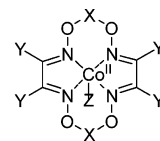
Materials. Monomers (styrene, BA, AMS, MMA, MAN) were obtained from Aldrich and were purified by filtration through alumina (to remove inhibitors) and flash distilled under vacuum immediately prior to use.

Reagent chemicals, 3,4-hexanedione (Aldrich, 95%), cobalt(II) chloride hexahydrate (Aldrich, 98%), sodium borohydride (Aldrich, 99%), and boron trifluoride etherate (Aldrich), were used without purification.

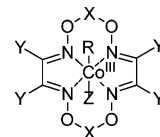
Initiators. azobis(isobutyronitrile) (AIBN) (Fluka) was purified by crystallization from chloroform/methanol; 1,1'-azobis(1-cyclohexanecarbonitrile) (ACHN) (DuPont VAZO-88) and 2,2'-azobis(2,4-dimethylpentane) (WAKO VR110) were used without purification.

The syntheses of $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$ ⁴⁸ and $^i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ ⁴⁹ are reported elsewhere.

AMS dimer (**6**) was supplied by NOF (Japan). The allyl sulfides, α -(*tert*-butylthiomethyl)styrene (**7**) and ethyl 2-(*tert*-butylthiomethyl)acrylate (**8**) were synthesized according to the literature procedures.⁵⁰



$\text{Co}^{\text{II}}(\text{DMG}-\text{BF}_2)_2$	$\text{X}=\text{BF}_2$	$\text{Y}=\text{CH}_3$	$\text{Z}=\text{methanol}$
$\text{Co}^{\text{II}}(\text{DMG})_2$	$\text{X}=\text{H}$	$\text{Y}=\text{CH}_3$	$\text{Z}=\text{pyridine}$
$\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$	$\text{X}=\text{BF}_2$	$\text{Y}=\text{Ph}$	$\text{Z}=\text{methanol}$



$^i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$	$\text{X}=\text{BF}_2$	$\text{Y}=\text{CH}_3$	$\text{R}=\text{CH}(\text{CH}_3)_2$	$\text{Z}=\text{H}_2\text{O}$
$\text{Bz}(\text{py})\text{Co}^{\text{III}}(\text{DMG})_2$	$\text{X}=\text{H}$	$\text{Y}=\text{CH}_3$	$\text{R}=\text{CH}_2\text{Ph}$	$\text{Z}=\text{pyridine}$
$\text{Me}(\text{py})\text{Co}^{\text{III}}(\text{DEG})_2$	$\text{X}=\text{H}$	$\text{Y}=\text{C}_2\text{H}_5$	$\text{R}=\text{CH}_3$	$\text{Z}=\text{pyridine}$
$\text{Me}(\text{py})\text{Co}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$	$\text{X}=\text{BF}_2$	$\text{Y}=\text{C}_2\text{H}_5$	$\text{R}=\text{CH}_3$	$\text{Z}=\text{pyridine}$
$\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$	$\text{X}=\text{BF}_2$	$\text{Y}=\text{C}_2\text{H}_5$	$\text{R}=\text{CH}_3$	$\text{Z}=\text{H}_2\text{O}$

$\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$. The [bis(μ -[(2,3-hexanedione dioximate)(2-)-*O,O'*]]tetrafluorodiborate(2-)-*N,N',N'',N'''*](methyl)-(aquo)cobalt [$\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$] was prepared following a procedure similar to that used previously for $^i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$.⁵¹

A solution of 3,4-hexanedione (5.3 g, 0.046 mol), hydroxylamine hydrochloride (5.3 g, 0.082 mol) in ethanol (53 mL), and pyridine (5 mL) was heated under reflux for 1 h and allowed to cool to ambient temperature when ice water (50 mL) was added. The gray crystals of 3,4-hexanedionedioxime that separated on standing at 0 °C were collected and recrystallized from ethanol (6.4 g, 95%). 3,4-Hexanedione dioxime (diethyl glyoxime, DEG) had mp 183–184 °C.

Sodium hydroxide (1.25 g, 0.031 mol in 50% aqueous solution) was added to a stirred solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3.2 g, 0.013 mol) and 3,4-hexanedione dioxime (4.6 g, 0.032 mol) in degassed methanol (70 mL) at room temperature. After 10 min, pyridine (1.02 mL, 0.013 mol) was added slowly. The reaction mixture was then cooled to –20 °C and stirred for 20 min under nitrogen. Then sodium hydroxide (0.81 g of 50% aqueous solution, 0.021 mol) and sodium borohydride (0.56 g, 0.015 mol) were added slowly. Iodomethane (1.09 mL, 2.48 g, 0.017 mol) was then added dropwise over 20 min, and the reaction mixture was allowed to warm to room temperature. The solution was concentrated under vacuum to ca. half its original volume and 40 mL of cold water was added. The precipitated $\text{Me}(\text{py})\text{Co}^{\text{III}}(\text{DEG})_2$ was isolated by filtration, washed with an aqueous solution of pyridine (5% v/v) and dried under vacuum over P_2O_5 to provide an orange powder (4.9 g, 82%) that was used directly as follows.

¹H NMR (CDCl_3): δ 0.8 (s, 3H, CoCH_3), 0.11–0.95 (m, 12H, CH_2CH_3), 2.6 (m, 8H, CH_2CH_3), 8–9.2 (m, pyridine).

$\text{Me}(\text{py})\text{Co}^{\text{III}}(\text{DEG})_2$ (3.6 g, 0.0082 mol) was added over 20 min to a solution of boron trifluoride etherate (9.2 g, 0.064 mol) in diethyl ether (5 mL) at –20 °C and the reaction mixture was allowed to warm to room temperature and the suspended $\text{Me}(\text{py})\text{Co}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$ was isolated by filtration, washed with ether and dried under vacuum to provide 3.2 g of orange-brown powder. A further 1.1 g was isolated after the filtrate was allowed to stand. Total yield was 4.3 g (98%).

Table 1. Properties of Polymers Formed in Feed Polymerization of Styrene with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate at 125 °C

time (min)	[Co(III)] initial ^a (M × 10 ⁴)	[Co(III)] feed ^b (M × 10 ⁴)	[ACHN] feed ^c (M)	[M] initial ^d	\bar{M}_n^e (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^f	convn (%)	[2] (%)
30	1.10	17.7	0.065	3.10	1050	2.18	<i>h</i>	0
60					1150	2.21	30	
120					1100	2.18	52	
ppt ^g	0.562	8.46	0.070	3.09	1630	1.69		0
60					2010	2.06	34	
120					1720	2.30	56	
ppt ^g	0.296	4.77	0.068	3.07	1940	2.03		0
60					3270	3.41	35	
120					2710	3.52	53	
ppt ^g	0	0	0.066	2.71	2750	3.26		0
60					32 200	1.70	28	
120					33 800	1.76	46	
180					38 100	1.68	58	
240					39 500	1.70	64	
300					37 400	1.81	75	
360					39 400	1.70	83	

^a Initial concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in reaction mixture. ^b Concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in initiator/complex feed. For details of conditions see Experimental Section. ^c Concentration of 1,1'-azobis(1-cyclohexanecarbonitrile) in feed. ^d Initial concentration of styrene in *n*-butyl acetate. Additional monomer added as feed; see Experimental Section. ^e Number-average molecular weight determined by GPC. ^f Molecular weight dispersity. ^g Precipitated (120 min) sample. ^h Not determined.

Table 2. Properties of Copolymers Formed in Feed Copolymerization of Styrene and AMS (~10:1 w/w) with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate at 125 °C

time (min)	[Co(III)] initial ^a (M × 10 ⁴)	[Co(III)] feed ^b (M × 10 ⁴)	[ACHN] feed ^c (M)	[M] initial ^d	\bar{M}_n^e (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^f	convn (%)	[2] ^g (%)
30	0.995	17.7	0.065	3.28	730	2.38	8	32
60					740	2.25	19	
120					690	2.06	34	
ppt ^h	0.537	8.84	0.064	3.28	1270	1.43		56
60					1170	2.17	24	
120					1040	2.21	40	
ppt ^h	0.295	4.77	0.071	3.26	1470	1.80		65
60					1370	2.11	22	
120					1270	2.11	39	
ppt ^h	0	0	0.066	2.90	1660	1.89		65
20					19 700	2.56	<i>i</i>	
40					14 900	2.55	<i>i</i>	
60					17 100	2.28	17	
120					24 400	1.72	30	
240					27 400	1.87	45	
360					29 400	1.80	68	

^a Initial concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in reaction mixture. ^b Concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in feed. For details of conditions, see Experimental Section. ^c Concentration of 1,1'-azobis(1-cyclohexanecarbonitrile) in feed. ^d Initial concentration of total monomers in *n*-butyl acetate. Additional monomer added as feed; see Experimental Section. ^e Number-average molecular weight determined by GPC. ^f Molecular weight dispersity. ^g Fraction of macromonomer chain ends (**2**) from ¹H NMR analysis (= 100.[**2**]/([**2**] + [**5**])). ^h Precipitated (120 min) sample. ⁱ Not determined.

¹H NMR (CDCl₃): δ 0.8 (s, 3H, CoCH₃), 1.0–1.2 (m, 12H, CH₂CH₃), 2.65 (m, 8H, CH₂CH₃), 8–9.2 (m, pyridine).

Me(py)Co^{III}(DEG-BF₂)₂ (3.2 g, 0.0060 mol) was added to degassed water under nitrogen at 30 °C. The solution was held at 30 °C for 40 min. The Me(aquo)Co^{III}(DEG-BF₂)₂ was isolated by filtration, washed with water, and dried to constant weight under vacuum. The bright orange powder (2.8 g, 99%) was used without further purification. ¹H NMR and reverse phase HPLC analysis indicated >95% purity.

¹H NMR (CDCl₃): δ 0.8 (s, 3H, CoCH₃), 1.0–1.1 (m, 12H, CH₂CH₃), 2.67 (q, 8H, CH₂CH₃), 4.8 (br s, 2H, H₂O). ¹H NMR (acetone-*d*₆): δ 1.0 (br s, 3H, CoCH₃), 1.2 (t, 12H, CH₂CH₃, *J* = 7.5 Hz), 2.85 (q, 8H, CH₂CH₃, *J* = 7.5 Hz), 4.9 (br s, 2H, H₂O).

A sample of MeCo^{III}(DEG-BF₂)₂ (15 mg) in acetone-*d*₆ (1 mL) was degassed by three freeze-thaw-evacuate cycles, sealed under vacuum (10⁻² mmHg), and heated at 80 °C for 69 h. NMR spectra were recorded after 1, 22, and 69 h. The NMR spectra were unchanged from the original spectrum.

A sample of MeCo^{III}DEG-BF₂ (16 mg) and AIBN (2.4 mg) in acetone-*d*₆ (1 mL) was degassed by three freeze-thaw-evacuate cycles, sealed under vacuum (10⁻² mmHg), and heated at 80 °C for 69 h. NMR spectra were recorded after 1,

22, and 69 h. The NMR spectra broadened substantially indicating formation of a paramagnetic Co(II) complex.

Polymerizations. Experiments Using a Monomer Feed. The following procedure is typical. Details of other experiments are provided in Tables 1–3.

The solvent, *n*-butyl acetate (20 g), in a 5 neck 250 mL reactor, equipped with condenser and a mechanical stirrer was purged with nitrogen. Styrene (10 g) and AMS (1 g) were added and the solution was purged with nitrogen for a further 10 min. The reactor was then heated to reflux (ca. 125 °C) and $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ (1.4 mg in 5 mL of degassed butyl acetate) added. The monomer (styrene 13.6 g and AMS 1.6 g at 0.139 mL/min) and initiator/transfer agent (1,1'-azobis(1-cyclohexanecarbonitrile), 0.93 g, $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$, 4.6 mg in degassed *n*-butyl acetate, 6.7 g at 0.063 mL/min) feeds were commenced immediately and completed over 120 min. The reaction mixture was then cooled. The reactor was sampled at regular intervals to monitor intermediate molecular weights (GPC) and conversions (¹H NMR). Precautions to exclude ingress of air were taken during all process and sampling steps. End groups were also determined on samples that were precipitated into a 20-fold excess of methanol. In this process some fractionation occurred on precipitation with loss of lower

Table 3. Properties of Copolymers Formed in Feed Copolymerization of Styrene and AMS (~5:1) with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate at 125 °C

time (min)	[Co(III)] ($\text{M} \times 10^4$) ^a	[Co(III)] feed ^b ($\text{M} \times 10^4$)	[ACHN] feed ^c (M)	[M] initial ^d	\bar{M}_n^e (g mol^{-1})	\bar{M}_w/\bar{M}_n^f	convn (%)	[2] ^g (%)
60	0.965	23.8	0.066	3.45	380	2.45	<i>i</i>	
120					410	2.10	<i>i</i>	
ppt ^h					1310	1.83		
60	0.498	9.10	0.067	3.44	810	2.06	10	
120					780	1.96	22	
ppt ^h					1180	1.53		68
60	0.270	4.68	0.066	3.42	1760	1.98	20	
120					1640	1.93	35	
ppt ^h					2140	1.60		>95
120	0.173			3.43	2660	1.87	20	
ppt ^h					3300	1.63		>70
60	0.090			3.43	4650	1.81	12	
ppt ^h					5160	1.64		>70
60	0	0	0.066	3.99	16 700	1.94	<i>i</i>	
120					19 500	1.79	<i>i</i>	
ppt ^h					19 600	1.83		

^a Initial concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in reaction mixture. ^b Concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in feed. For details of conditions, see Experimental Section. ^c Concentration of 1,1'-azobis(1-cyclohexanecarbonitrile) in feed. ^d Initial concentration of total monomers in *n*-butyl acetate. Additional monomer added as feed; see Experimental Section. ^e Number-average molecular weight determined by GPC. ^f Molecular weight dispersity. ^g Percentage of macromonomer chain ends (**2**) from ¹H NMR analysis ($= 100 \cdot [\text{2}]/([\text{2}] + [\text{5}])$). ^h Precipitated (60 or 120 min) sample. ⁱ Not determined.

Table 4. Properties of Copolymers Formed in Batch Copolymerization of Styrene and AMS (~10:1) with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate

temp (°C)	[styrene] (M)	[AMS] (M)	[Co]/[M] ^c $\times 10^{-5}$	\bar{M}_n^d (g mol^{-1})	\bar{M}_w/\bar{M}_n^e	convn (%)	[2] ^f (%)
125 ^a	2.53	0.257	0	64 500	1.7		
	2.47	0.251	1.89	1410	1.8	54	70
	2.42	0.246	3.77	750	1.8	39	56
	2.32	0.236	7.54	450	1.6	36	52
80 ^b	2.38	0.242	0	32 600	2.0		
	2.33	0.237	1.84	1460	1.6	45	70
	2.28	0.232	3.70	1090	1.5	33	50
	2.19	0.223	7.39	660	1.3	22	33

^a 2,2'-Azobis(2,4-dimethylpentane) initiator. ^b 1,1'-Azobis(4-cyclohexanecarbonitrile) initiator. ^c Ratio of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ to total monomer concentration. ^d Number-average molecular weight determined by GPC. ^e Molecular weight dispersity. ^f Percentage macromonomer chain ends (**2**) from ¹H NMR analysis ($= 100 \cdot [\text{2}]/([\text{2}] + [\text{5}])$).

Table 5. Properties of Copolymers Formed in Batch Copolymerization of Styrene and AMS (10:1) with Various Cobalt Complexes in *n*-Butyl Acetate at 125 °C and 2,2'-Azobis(2,4-dimethylpentane) Initiator (0.0003 M)²⁹

complex	[styrene] (M)	[AMS] (M)	[Co]/[M] ^d $\times 10^{-5}$	\bar{M}_n^e (g mol^{-1})	\bar{M}_w/\bar{M}_n^f	convn (%)	[2] ^g (%)
control	2.48	0.248	0	58 300	1.80	13	
DMG ^a	2.48	0.248	6.1	1060	1.62	19	0.71
control	2.48	0.248	0	72 300	1.73	15	
DEG ^b	2.48	0.248	6.1	1390	1.70	19	0.85
control	2.46	0.246	0	71 900	1.70	12	
DPG ^c	2.46	0.246	6.1	1450	1.74	23	0.91

^a $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$. ^b $\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$. ^c $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$. ^d Ratio of cobalt complex concentration to total monomer concentration. ^e Number-average molecular weight determined by GPC. ^f Molecular weight dispersity. ^g Mole fraction of macromonomer chain ends (**2**) from ¹H NMR analysis ($= [\text{2}]/([\text{2}] + [\text{5}])$).

molecular weight material. The results of this experiment (molecular weights, end group purities) are provided as the first set of entries in Table 2.

The rate of monomer feed was chosen such that the concentration of polymer did not exceed 30 wt % of monomer to minimize further reaction of the formed macromonomer. The initial concentration of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ and the feed rate were chosen so as to maintain the molecular weight by keeping the ratio $[i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2]/[\text{total monomers}]$ approximately constant. The results of these experiments are presented in Tables 1–3.

Batch Polymerization Procedure. Stock solutions of the monomers, initiator, and the cobalt complex in *n*-butyl acetate were prepared and appropriate aliquots transferred to ampoules which were degassed through four freeze–evacuate–thaw cycles. The ampoules were sealed under vacuum and heated in a thermostated bath for the requisite times. The ampoules were then rapidly cooled, opened and the solvent and excess monomers were removed under vacuum to provide a residue

that was analyzed by ¹H NMR and GPC. No precipitation or fractionation was performed. Details of concentrations and reaction conditions used are provided in Tables 4–9. The molecular weights given in the tables for samples with $\bar{M}_n < 600$ are an overestimate because of the interference from peaks in the chromatogram due to low molecular weight impurities (e.g. solvent, monomer, cobalt complex, etc.).

The typical procedure was as follows:

A mixture of styrene (1.3 g, 12.5 mmol), α -methylstyrene (0.15 g, 1.27 mmol) (molar monomer ratio 10/1), *n*-butyl acetate (3 g), 2,2'-azobis(2,4-dimethylpentane) (8.9×10^{-5} g), and the appropriate amount of $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ (to provide the concentration shown in Table 4) was placed in each of four ampoules which were degassed by four freeze–evacuate–thaw cycles. The ampoules were then sealed and the polymerization mixtures heated at 125 °C for 2 h. The ampoules were then cooled rapidly and opened. A sample of each polymerization mixture ($\sim 10 \mu\text{L}$) was transferred to a NMR tube, diluted with CDCl_3 (~ 0.5 mL) and analyzed by ¹H NMR to determine the

Table 6. Properties of Copolymers Formed in Batch Copolymerization of BA and AMS Copolymerization with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate

temp (°C) (BA:AMS) ^a	[BA] (M)	[AMS] (M)	[Co]/[M] ^d × 10 ⁻⁵	\bar{M}_n^e (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^f	convn (%)	AMS ^g	[2] ^h
125 ^b (~50:1)	2.62	0.044	0	18 900	1.85	6	0.05	
	2.56	0.043	1.91	3460	2.10	43	0.05	1
	2.51	0.042	3.81	1950	1.92	32	0.06	0.87
	2.41	0.041	7.61	1620	1.81	30	0.06	0.77
	2.23	0.038	15.22	1200	1.72	21	0.07	0.73
125 ^b (~25:1)	1.93	0.033	30.41	1070	1.65	21	0.06	<i>i</i>
	2.62	0.089	0	18 100	1.77	13	0.17	
	2.56	0.087	1.88	2230	2.10	20	0.2	1
	2.51	0.085	3.75	1400	1.68	13	0.13	1
	2.41	0.081	7.49	1200	1.73	13	0.13	0.93
80 ^c (~50:1)	2.22	0.075	14.97	1070	1.58	12	0.12	0.85
	2.91	0.047	0	56 100	1.76	14	0.12	
	2.83	0.046	1.73	1880	1.96	11	0.10	1
	2.78	0.045	3.44	1600	1.82	11	0.10	1
	2.67	0.043	6.88	1480	1.80	13	0.09	0.91
80 ^c (~25:1)	2.47	0.040	13.77	1210	1.76	10	0.09	0.85
	2.15	0.035	27.55	1170	1.64	10	0.09	0.8
	2.72	0.093	0	41 400	1.69	9	0.17	
	2.67	0.090	1.81	1150	1.48	7	0.2	1
	2.61	0.088	3.59	1060	1.42	6	0.18	1
80 ^c (~10:1)	2.50	0.085	7.20	960	1.39	5	0.17	0.96
	2.29	0.078	14.41	940	1.37	6	0.15	0.91
	2.30	0.187	0	28 200	1.64	4	0.38	
	2.25	0.183	2.03	640	1.33	5	0.36	1
	2.20	0.179	4.06	610	1.31	5	0.35	1
80 ^c (~5:1)	2.11	0.172	8.12	550	1.27	3	0.36	1
	2.24	0.365	0	23 500	1.75	3	0.39	
	2.18	0.355	1.94	500	1.20	4	0.41	1
	2.15	0.350	3.86	490	1.20	4	0.38	1
	2.07	0.337	7.71	480	1.20	3	0.43	1

^a Nominal ratio of monomers in parentheses. ^b Initiator was 2,2'-azobis(2,4-dimethylpentane) (3.74×10^{-4} g). ^c Initiator was azobis(isobutyronitrile) (3.74×10^{-4} g). ^d Ratio of cobalt complex concentration to total monomer concentration. ^e Number-average molecular weight determined by GPC. ^f Molecular weight dispersity. ^g Mole fraction of AMS in copolymer. ^h Mole fraction of macromonomer chain ends (**2**) from ¹H NMR analysis ($=[\text{2}]/([\text{2}] + [\text{5}])$). Value of "1" indicates that the end groups (**5**) were not detectable by ¹H NMR (i.e., >97% (**2**)). ⁱ Not determined.

Table 7. Properties of Copolymers Formed in Batch Copolymerization of BA and MMA (~10:1) with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in *n*-Butyl Acetate

temp °C	[BA] (M)	[MMA] (M)	[Co]/[M] ^c × 10 ⁻⁵	\bar{M}_n^d (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^e	convn (%)	MMA ^f	[2] ^g
80 ^a	1.73	0.168	0	75 500	2.08	54	0.14	
	1.69	0.164	2.67	12 120	1.82	53	0.14	1
	1.65	0.161	5.34	2600	1.66	21	0.17	0.94
	1.59	0.154	11.0	1500	1.50	9	0.18	0.92
	1.47	0.143	21.0	1200	1.43	10	0.17	0.86
	1.28	0.124	43.0	920	1.31	8	0.14	0.75
125 ^b	1.73	0.168	0	10 400	2.56	76	0.11	
	1.69	0.164	2.67	3510	1.74	45	0.14	0.93
	1.65	0.161	5.34	1990	1.7	32	0.15	0.92
	1.59	0.154	11.0	1220	1.6	14	0.17	0.91
	1.47	0.143	21.0	1030	1.73	15	0.15	0.87
	1.27	0.124	43.0	830	1.51	9	0.14	0.79

^a Initiator was 2,2'-azobis(2,4-dimethylpentane) (3.74×10^{-4} g). ^b Initiator was azobis(isobutyronitrile) (3.74×10^{-4} g). ^c Ratio of cobalt complex concentration to total monomer concentration. ^d Number-average molecular weight determined by GPC. ^e Molecular weight dispersity. ^f Mole fraction of MMA in copolymer. ^g Fraction of macromonomer chain ends (**2**) from ¹H NMR analysis ($=[\text{2}]/([\text{2}] + [\text{5}])$). Value of "1" indicates that the end groups (**5**) were not detectable by ¹H NMR (i.e., >97% (**2**)).

monomer conversion. The unconverted monomer and solvent removed under vacuum ($\sim 10^{-1}$ mmHg) at <40 °C to provide a residue that was analyzed by ¹H NMR and GPC. The results of these experiments are shown in Table 4.

Structures **9** (AMS-co-S), **10** (BA-co-AMS), **11** (BA-co-MAN), and **12** (BA-co-MMA) are used to refer to the products of copolymerizations. The polymer chain will in each case be a copolymer chain. The end groups shown are the predominant end groups. The structures **a** and **c** are formed by H-transfer to the monosubstituted monomer (BA or S). Structures **b** and **d** are formed by H transfer to the α -methylvinyl monomer (AMS, MMA). Structures **a** and **b** have a terminal unit derived from the α -methylvinyl monomer. Structures **c** and **d** have a terminal unit derived from the monosubstituted monomer.

Characterization of Copolymers. Poly(AMS-co-S) (9). The ¹H NMR spectra of S/AMS copolymers made by catalytic

chain transfer have been published elsewhere.³⁵ The unsaturated end groups give rise to signals in the ¹H NMR spectrum (CDCl₃) as follows: AMS-derived terminal methylene double bond (**13**), δ 4.8, 1H and δ 5.2, 1H, $-\text{C}(\text{Ph})=\text{CH}_2$; 1,3-diphenylpropen-3-yl end group (**14**), δ 6.1–6.3, 2H, $-\text{CH}(\text{Ph})-\text{CH}=\text{CH}-\text{Ph}$ and δ 3.1, 1H, $-\text{CH}(\text{Ph})-\text{CH}=\text{CH}-\text{Ph}$. The ratio of the signals at δ 3.1 and δ 4.8 gave the best estimate of terminal double bond content. In a previous report³⁵ it was suggested the signals at δ 6.1–6.3 were due to only one hydrogen of **14** with the other appearing within the aromatic envelope. It has now been established by 2D NMR (COSY) on a sample of **14** (precipitated sample with \bar{M}_n 1630, refer to Table 1, first-mentioned experiment) that both olefinic resonances appear at δ 6.1–6.2 (Figure 1). Integration supports this assignment. The signals at δ 6.1–6.3 ($-\text{CH}(\text{Ph})-\text{CH}=\text{CH}-\text{Ph}$), δ 3.1 ($-\text{CH}(\text{Ph})-\text{CH}=\text{CH}-\text{Ph}$), and δ 0.9–1.1 ($-\text{CH}_2-$

Table 8. Properties of Copolymers Formed in Batch Copolymerization of BA and MAN (10:1) with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ in n -Butyl Acetate at 125 °C^a

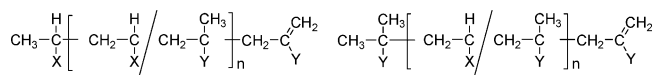
[BA] (M)	[MAN] (M)	[Co]/[M] ^b × 10 ⁻⁵	\bar{M}_n^c (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^d	convn (%)	[2] ^e
1.84	0.179	0	9300	1.90	8	
1.80	0.175	2.50	1300	1.54	8	0.81
1.76	0.171	4.99	1040	1.62	8	0.76
1.69	0.164	10.0	960	1.49	8	0.80
1.56	0.152	20.0	800	1.47	7	0.87
1.36	0.132	40.0	670	1.50	6	0.86

^a Initiator was 2,2'-azobis(2,4-dimethylpentane) (3.74×10^{-4} g). ^b Ratio of cobalt complex concentration to total monomer concentration. ^c Number-average molecular weight determined by GPC. ^d Molecular weight dispersity. ^e Fraction of macromonomer chain ends (2) from ¹H NMR analysis (= [2]/([2] + [5])). Value of "1" indicates that the end groups (5) were not detectable by ¹H NMR (i.e., >97% (2)).

Table 9. Properties of Copolymers Formed in Batch Copolymerization of BA and AMS Copolymerization (~50:1) with Various Complexes in n -Butyl Acetate at 125 °C^{a,b}

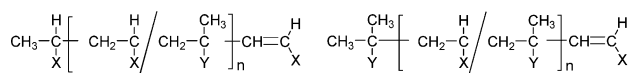
complex	[BA] (M)	[AMS] (M)	[Co]/[M] ^c × 10 ⁻⁵	\bar{M}_n^f (g mol ⁻¹)	\bar{M}_w/\bar{M}_n^g	convn (%)	AMS ^h	[2] ⁱ
DPG ^c	2.31	0.046	0	104 700	2.07	17	0.09	
	2.27	0.045	2.106	5400	2.10	3	0.13	1
	2.23	0.045	4.225	1960	1.73	1	0.14	1
	2.16	0.043	8.44	1820	1.71	1	0.13	1
	2.03	0.041	16.86	1420	1.64	1	0.12	1
DEG ^d	1.81	0.036	33.75	1260	1.58	1	0.11	1
	2.31	0.046	0	49 300	1.74	11	0.12	1
	2.28	0.046	2.07	2370	1.85	11	0.13	1
	2.26	0.045	4.13	1650	1.70	10	0.12	1
	2.21	0.044	8.26	1160	1.66	5	0.12	1
	2.11	0.042	16.58	1130	1.57	4	0.12	1

^a Initiator was 2,2'-azobis(2,4-dimethylpentane) (3.74×10^{-4} g). ^b Results for similar polymerizations with $i\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ are presented in Table 6. ^c $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$. ^d $\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$. ^e Ratio of cobalt complex concentration to total monomer concentration. ^f Number-average molecular weight determined by GPC. ^g Molecular weight dispersity. ^h Mole fraction of AMS in copolymer. ⁱ Mole fraction of macromonomer chain ends (2) from ¹H NMR analysis (= [2]/([2] + [5])). Value of "1" indicates that the end groups (5) were not detectable by ¹H NMR (i.e., >97% (2)). ^e Fraction of AMS in copolymer.



9a X=Ph, Y=Ph

9b X=Ph, Y=Ph

10a X=CO₂Bu, Y=Ph10b X=CO₂Bu, Y=Ph11a X=CO₂Bu, Y=CN11b X=CO₂Bu, Y=CN12a X=CO₂Bu, Y=CO₂Me12b X=CO₂Bu, Y=CO₂Me

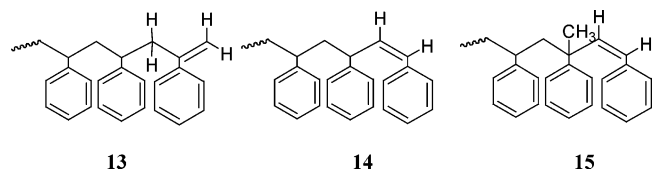
9c X=Ph, Y=Ph

9d X=Ph, Y=Ph

10c X=CO₂Bu, Y=Ph10d X=CO₂Bu, Y=Ph11c X=CO₂Bu, Y=CN11d X=CO₂Bu, Y=CN12c X=CO₂Bu, Y=CO₂Me12d X=CO₂Bu, Y=CO₂Me

CH(Ph)/CH₃) appear in a 2:1:3 ratio. This COSY spectrum also enables us to assign a signal at δ 2.3 on the fringe of the aliphatic envelope to $-\text{CH}_2\text{CH}(\text{Ph})\text{CH}_3$.

The use of the signals at δ 6.1 for integration is complicated by its proximity to the broad aromatic resonance at δ 7.6–7.2. The signal at δ 3.1 may be low if the internal double bond product is a mixture of 14 and 15. However, the yield of 15 is anticipated to be small.



13

14

15

BA Copolymers (10–12). Examples of ¹H NMR spectra of BA/AMS copolymers have been published elsewhere.³⁹ The internal double bond of the unsaturated butyl acrylate-derived chain end (10–12c,d) gives rise to a relatively sharp "doublet" at δ 5.8 ($-\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$) and a broader multiplet at δ 7.0 ($-\text{CH}=\text{CH}-\text{CO}_2\text{Bu}$). Fractions of α -methylvinyl monomer-

derived chain ends [2] (= [2]/([2] + [5])) shown in the tables are based on the ratio of the areas of the signal at δ 5.8 and those assigned to the $-\text{CH}_2-\text{C}(\text{Y})=\text{CHH}$ end of the macromonomer (10–12a,b).

A more comprehensive study of the NMR of 9 has recently been published by Chui et al.³⁹ The comparatively high levels of AMS used by Chui et al.³⁹ mean that unsaturated chain ends derived from BA were not observed.

Poly(AMS-co-BA) Macromonomer (10a,b). ¹H NMR (acetone-*d*₆): δ 0.9, butyl CH₃; 1.0–2.3, butyl, backbone H; 2.55, $-\text{CH}_2-\text{C}(\text{Ph})=$; 3.95, OCH₂; 5.0, =CHH; 5.2, =CHH; 7.15–7.25, ArH.

Poly(MAN-co-BA) Macromonomer (11a,b). ¹H NMR (CDCl₃): δ 0.95, butyl CH₃; 1.0–2.3, butyl, backbone H; 2.6, $-\text{CH}_2-\text{C}(\text{CN})=$; 4.0, OCH₂; 5.7, =CHH; 5.85, =CHH.

Poly(MMA-co-BA) Macromonomer (12a,b). ¹H NMR (CDCl₃): δ 0.9, butyl CH₃; 1.0–2.3, butyl, backbone H; 2.55, $-\text{CH}_2-\text{C}(\text{CO}_2\text{CH}_3)=$; 3.6, OCH₃; 4.0, OCH₂; 5.5, =CHH; 6.15, =CHH.

Macromonomer Chain Transfer Agents. Macromonomer 16. Styrene (40 mL), AIBN (0.110 g) and allyl sulfide 7 (5 g) were dissolved in benzene (40 mL). The mixture was degassed using four freeze–pump–thaw cycles, sealed under vacuum and heated at 60 °C for 64 h. The ampules was then cooled, opened, the solvent was removed on a rotary evaporator and the residue precipitated into methanol (\bar{M}_n 1710, \bar{M}_w/\bar{M}_n 1.94). The precipitate was redissolved in ethyl acetate and precipitated into methanol for a total of five precipitations to yield 12.3 g (34% conversion) of macromonomer 16 with \bar{M}_n 2380 and \bar{M}_w/\bar{M}_n 1.53. NMR analysis demonstrated no residual 7.

Macromonomer 17. A solution of styrene (10 g) and allyl sulfide 8 (1.63 g) in butyl acetate (30 g) was degassed under nitrogen in a multinecked 250 mL reactor equipped with a mechanical stirrer. The mixture was heated to reflux (125 °C) under nitrogen and the two feeds (feed 1, allyl sulfide 8 (6.67 g) in styrene (40 g) at 0.21 mL/min; feed 2, the initiator ACHN (283 mg) in butyl acetate (20 g) at 0.063 mL/min) added by syringe pump. After 240 min, the macromonomer 17 (\bar{M}_n 1890,

Table 10. Transfer Constants (C_T) of $\text{Co}^{\text{II}}(\text{DMG}-\text{BF}_2)_2$ in Polymerizations of Selected Monomers

monomer	C_T	solvent	T (°C)	ref
BA ^a	~45	BuAc/MMA	60	this work
	~65		80	
	~90		125	
BA ^b	~650		60	54
styrene ^a	1500	bulk	60	55
styrene ^a	1027	bulk	40	38
	533		50	
	660		60	
	265		70	
	2700	BuAc	125	
styrene ^a	~2000	BuAc/AMS	80	this work
	~1500	BuAc/AMS	125	
	3–7000	bulk	60	
styrene ^b	~8–9000	bulk	60	53,54
MMA	24 300	33%(v/v) in toluene	60	55
MMA	36 140	bulk	60	55
MMA	17 900	toluene	60	78
MMA	33 500	bulk	60	74,76
	32 800		70	
	35 200		80	
	32 500		90	
	33 000		40	
	39 000		50	
	34 000		60	
MMA	27 000	bulk	70	74
	39 800		60	
	28 000		60	
BMA	28 000	bulk, toluene	60	90
AMS	815 000	bulk	40	38
	893 000		50	
AMS	~500 000	BuAc/styrene	80	this work
	~300 000		125	
AMS	~70 000	BuAc/BA	80	this work
	~100 000		125	

^a Apparent transfer constant with monosubstituted monomers should be considered as a lower limit due to reversible consumption of the cobalt complex under the reaction conditions (see text).

^b Value dependent on initiator concentration. ^c Estimated value of transfer constant after allowing for reversible consumption of the cobalt complex.

\bar{M}_w/\bar{M}_n 1.58) was isolated by two precipitations into acidified methanol. The conversion based on isolated macromonomer was 50%.

Macromonomer Transfer Constants. Aliquots of a stock solution of the initiator (AIBN at 60 or 80 °C; *tert*-butyl peroxybenzoate at 100 or 120 °C) in monomer were transferred to ampules containing the appropriate amount of macromonomer (**9**, **16**, or **17**) or α -methylstyrene dimer (**6**) in monomer which were then degassed through three freeze–evacuate–thaw cycles. The ampules were sealed under vacuum and heated in a thermostated bath for the requisite times. The ampules were then cooled, opened and the solvent and excess monomers were removed under vacuum to provide a residue that was analyzed by GPC. No precipitation or fractionation was performed. Reaction conditions were chosen to provide conversions of <10%. Reaction conditions and molecular weight data are summarized in Table 12. Values of transfer constants evaluated by analysis of the chain length distributions according to the log CLD method are provided in Table 13. The typical procedure was as follows:

Aliquots (5 mL) of a solution on *tert*-butyl perbenzoate (11.4 mg in styrene 25 mL, 3.4 M) were added to each of four ampules containing macromonomer **17** (0, 24.5 mg, 50.9 mg, 74.9 mg respectively). The ampules were degassed through three freeze–evacuate–thaw cycles. The ampules were then sealed under vacuum and heated in a thermostated bath at 120.0±0.1 °C for 30 min. The ampules were then cooled rapidly, opened and the remaining monomer removed under vacuum at 30 °C. The monomer conversions were <10%. The molecular weights determined by GPC analysis are reported in Table 12. The transfer constant evaluated from these data is given in Table 13.

Table 11. Reactivity Ratios (r_A , r_S) and Propagation-depropagation Equilibrium Constants (K) for Selected Monomer Pairs

monomer A	monomer S	r_A	r_S	K	T (°C)	ref
MMA	BA	2.24	0.414		50	62
		1.789	0.298			91
		3.26	0.43		50	92
		2.24	0.38		80	93
		1.62	0.37		120	93
MAN	BA	2.68	0.33			^b
		2.28	0.55			^c
AMS	BA	0.67	0.096			^b
		0.31	0.20			^c
		0.149	0.153		80	68
		0.022	0.166		120	68
		0.557	0.148	6.1	80	^e , 69
MAN	styrene	0.502	0.171	22.0	120	^e , 69
		0.32	0.39		60	94
		0.41	0.37		90	
		0.42	0.38		120	
		0.14	10.1		–20	95
AMS	styrene ^a	0.15	1.0	7.1	60	67
		0.3	1.09	17.2	90	
		0.4	1.13	28.5	110	
		0.8	1.2	67	150	
		0.3	0.5	1.7	20	96
AMS	MMA	0.4	0.55	5.1	50	
		0.35	0.55	7.1	60	
		0.2	0.6	12.9	80	
		0.05	0.65	22.9	100	

^a Values calculated using the relationship $\log r_A = 2.48 - 1094/T$, $\log r_S = 0.378 - 125/T$.⁶⁷ ^b Estimated from $Q - e$ values.^{70,72}

^c Estimated using the patterns of reactivity scheme.⁷¹ ^d K is the rate constant for AMS depropagation relative to cross propagation, in bulk BA-AMS copolymerization⁶⁹ obtained using the Kruger model.⁷³

Results and Discussion

A series of binary copolymerizations of a monosubstituted monomer (styrene or BA) with an α -methylvinyl monomer (MMA, MAN, or AMS) in the presence of a chain transfer catalyst were performed. Alkylcobalt(III) complexes (e.g., $^i\text{Pr}-\text{Co}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$) were used in most of the polymerizations reported in this paper. These complexes undergo unimolecular homolysis ($^i\text{Pr}-\text{Co}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ —Scheme 5) or radical induced decomposition ($\text{Me}-\text{Co}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$ —Scheme 6) to produce the corresponding cobalt(II) complex as the active transfer agent under polymerization conditions.⁹ The cobalt(III) complexes are preferred over the analogous cobalt(II) complexes as they are substantially less air sensitive particularly in solution and this simplifies the protocol for setting up the reactions. Generation of the active cobalt(II) species should not be rate limiting at temperatures >60 °C. In general, conditions were chosen so as to give low molecular weights (\bar{M}_n in range 500–5000). The polymers formed were analyzed by GPC for molecular weight and by ^1H NMR for end group composition. These results are summarized in Tables 1–9.

Good molecular weight control was observed in copolymerizations of styrene with AMS (see Figures 2–4 and Tables 1–4). A first series of experiments (Tables 1–3) was conducted using a feed addition protocol (See Experimental Section) under which monomers and transfer agent were fed to a stirred reactor at a rate such that the macromonomer molecular weight should remain constant by keeping the ratio $[\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2]:[\text{total monomers}]$ approximately constant. This strategy also maintained polymer concentration at <30 wt % vs monomer thus minimizing the likelihood that

Table 12. Molecular Weights Obtained in Styrene Polymerizations in the Presence of Macromonomer Chain Transfer Agents (9, 16, 17) and AMS Dimer (6)^a

transfer agent	temp (°C)	[CTA] (M × 10 ²)	\bar{M}_n^k (g mol ⁻¹)	\bar{M}_w/\bar{M}_n
9^a	100	0	265 000	1.76
	100	2.197	222 000	1.72
	100	4.376	183 000	1.74
9^b	100	6.513	191 000	1.68
	120	0	224 000	2.21
	120	2.085	209 000	1.74
	120	4.333	146 000	2.00
	120	6.538	97 000	1.86
16^c	80	0	64 600	1.65
	80	1.09	70 900	1.50
	80	2.15	69 400	1.45
	80	3.14	68 400	1.42
16^d	120	0	180 000	2.25
	120	1.016	169 000	1.64
	120	2.098	147 000	1.59
	120	3.164	133 000	1.60
17^e	80	0	67 400	1.59
	80	1.31	70 800	1.47
	80	2.64	68 600	1.44
	80	4.01	66 800	1.43
17^f	120	0	125 000	1.83
	120	1.357	115 000	1.70
	120	2.707	97 100	1.63
	120	3.984	88 600	1.57
17/BMA^g	120	0	567 700	1.90
	120	1.340	315 000	1.86
	120	2.660	178 100	1.86
	120	4.048	156 400	1.80
AMS dimer (6)^h	80	0	93 900	1.63
	80	9.689	38 700	1.86
	80	17.73	25 600	1.70
	80	25.09	19 100	1.70
AMS dimer (6)ⁱ	100	0	387 600	1.81
	100	8.335	43 800	2.03
	100	17.18	17 700	2.18
	100	24.71	14 400	1.89
AMS dimer (6)^j	120	0	140 100	1.90
	120	9.520	24 400	2.21
	120	17.01	15 500	2.11
	120	25.89	1180	1.93

^a Initiators used *tert*-butyl perbenzoate (tBPB) and azobisisobutyronitrile (AIBN). The reaction time and initiator concentrations provided in footnotes b–k. ^b 147 min, tBPB 3.43×10^{-3} M. ^c 35 min, tBPB 2.951×10^{-3} M. ^d 80 min, AIBN 6.18×10^{-3} M. ^e 32 min, tBPB 3.40×10^{-3} M. ^f 80 min, AIBN 6.28×10^{-3} M. ^g BMA polymerization, 30 min, tBPB 3.40×10^{-3} M. ^h 31 min, tBPB 6.08×10^{-4} M. ⁱ 90 min, tBPB 6.22×10^{-3} M. ^j 180 min, AIBN 2.95×10^{-3} M. ^k 46 min, tBPB 3.07×10^{-3} M. ^l Values provided to 3 significant figures.

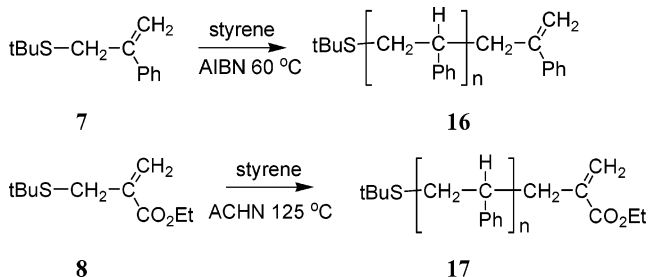
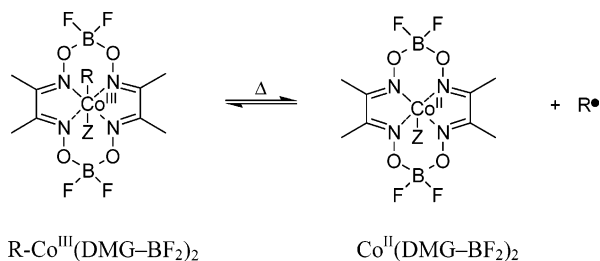
the macromonomers **2** would undergo further reaction by copolymerization or chain transfer (see later discussion). The polymerizations were carried out at 125 °C (*n*-butyl acetate at reflux) with continuous addition of a rapidly decomposing initiator [ACHN; $t_{1/2}$ at 125 °C ~ 5 min] to maintain the polymerization rate. Thermal initiation also occurs under these conditions. However, the relative importance of the two initiation processes was not quantified.

A second set of experiments was conducted in sealed ampules at 80 or 125 °C and only taken to low conversion of monomer (Table 4). Slightly higher molecular weights and slightly lower end group purities were observed in the sealed tube experiments. Given the difference in reaction conditions and that end group analysis on the product from the feed experiments was carried out on precipitated samples, the agreement between the experiments is considered within experimental error.

Table 13. Transfer Constants (C_T) Measured for Macromonomer Transfer Agents (9, 16, 17) and AMS Dimer (6) Determined by log CLD Method

transfer agent	monomer	temp (°C)	C_T (this work)	$C_T^{a,89}$	$C_T^{a,79}$
AMS dimer (6)	sty	60	0.24 ^c	0.16	
		80	0.27	0.23	
		100	0.25	0.26	
		110		0.28	0.20 ^b
		120	0.28	0.36	
		130		0.48	
macromonomer 9^c	BMA	120	0.09		
	MMA	110			0.13
	sty	100	0.03		
macromonomer 16^d	sty	120	0.16		
	sty	80	~0		
macromonomer 17^e	sty	120	0.11		
	sty	80	~0		
	sty	120	0.15		
	BMA	120	0.14		

^a Determined by Mayo method. ^b A mixed MMA–AMS dimer was reported to have a similar transfer constant (0.19 with styrene, 0.10 with MMA).⁷⁹ ^c Styrene macromonomer **9**, \bar{M}_n 1180, prepared by copolymerization of AMS with Sty and 50 ppm of Co(III). Value takes into account the end group purity ($= [2]/([2] + [5]) \times 100$) of 68% estimated by NMR (see Table 3). ^d Styrene macromonomer **16**, \bar{M}_n 2380, prepared by addition–fragmentation chain transfer with corresponding allyl sulfide **7**. ^e Styrene macromonomer **17**, \bar{M}_n 1880, prepared by addition–fragmentation chain transfer with corresponding allyl sulfide **8**.

Scheme 4**Scheme 5^a**

^a Z is solvent.

The product of styrene–AMS copolymerization contained a mixture of end group structures **2** and **5** (Tables 1–4). The absolute number of end groups determined by NMR (see Experimental Section) was in accord with that expected on the basis of the GPC determined molecular weight. By selecting the ratio of AMS:styrene and the cobalt concentration, conditions could be chosen such that product **2** dominates (favored by high AMS concentration and low cobalt concentration (see Tables 1–4) and **5** is not detectable by ¹H NMR. End group compositions observed in the sealed tube experiments conducted at 125 and 80 °C are shown in Figure 3 and Figure 4, respectively. Higher macromonomer purity (greater amount of **2**) was observed for the higher reaction temperature. The temperature effect may in

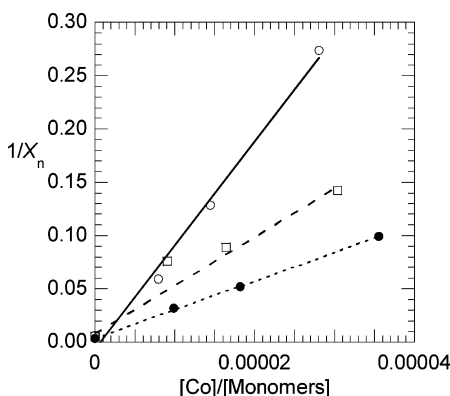
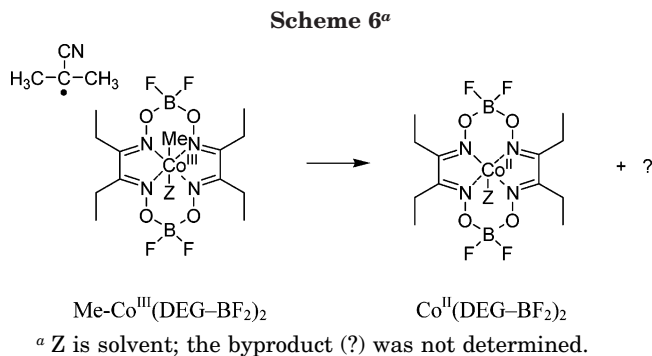


Figure 2. “Mayo” plot (reciprocal degree of polymerization ($1/\bar{X}_n$) vs [catalyst]/[total monomers]) for styrene-AMS feed copolymerization at 125 °C in the presence of $\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ with [styrene]:[AMS] (a) $\sim 100:0$ (●, - -), (b) $\sim 90:10$ (□, - -), (c) $\sim 80:20$ (○, - -). Experimental conditions are summarized in Tables 1–3.

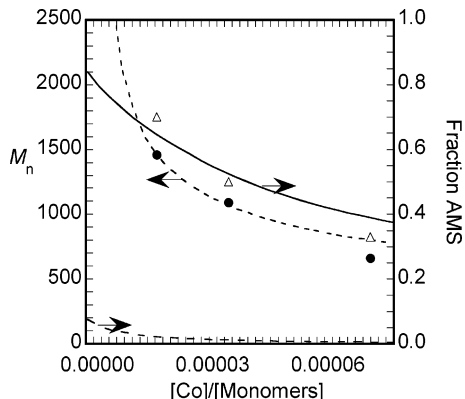


Figure 3. Comparison of observed and predicted properties of styrene-AMS formed in copolymerization ([styrene]:[AMS] $\sim 5:1$) in the presence of $\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 80 °C: (a) fraction of AMS-derived chain ends $[2]/([2] + [5])$ (experimental, ●; predicted, - -), (b) predicted fraction of AMS in copolymer (- -), and (c) number-average molecular weight (\bar{M}_n experimental, Δ; \bar{M}_n predicted, -). Experimental conditions are summarized in Table 4. Parameters used in the fit are given in Table 14.

large part be associated with the temperature dependence of the reactivity ratios (see below).

Good molecular weight control was also observed in homopolymerization of styrene at 125 °C (Table 1). No dependence of conversion on cobalt concentration was seen and no broadening of molecular weight distribution was observed for higher conversions (See Table 1). Many previous studies on catalytic chain transfer in styrene polymerization at lower reaction temperatures have indicated that inhibition periods, catalyst poisoning and/or retardation complicate the polymerization.^{27,28} These

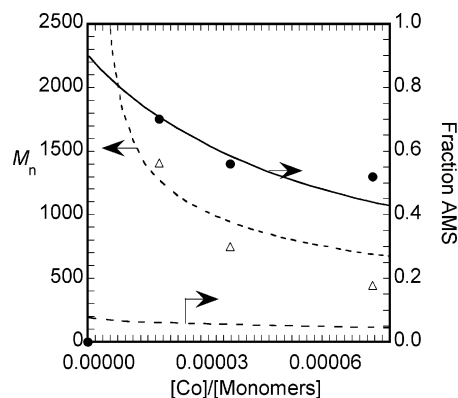


Figure 4. Comparison of observed and predicted properties of styrene-AMS formed in copolymerization ([styrene]:[AMS] $\sim 5:1$) in the presence of $\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 125 °C: (a) fraction of AMS-derived chain ends $[2]/([2] + [5])$ (experimental, ●; predicted, - -), (b) predicted fraction of AMS in copolymer (- -), and (c) number-average molecular weight (\bar{M}_n experimental, Δ; \bar{M}_n predicted, -). Experimental conditions are summarized in Table 4. Parameters used in the fit are given in Table 14.

phenomena have been associated with the reversible formation of a polystyryl-cobalt(III) species.^{28,52–54} At 125 °C, there may be less formation of such species or the reaction may be more readily reversible. The estimated transfer constant to styrene (ca. 2700, from Mayo plot shown in Figure 2) appears approximately 2-fold higher than that reported^{38,55} at lower temperatures with the corresponding cobalt(II) complex (see Table 10). However it is still significantly lower than the estimated value of transfer constant after allowing for reversible consumption of the cobalt complex.^{53,54}

The following expression, eq 1a, which defines the meaning of the average transfer constant \bar{C}_{tr} as may be derived from a Mayo plot of $1/\bar{X}_n$ vs total monomer concentration.

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{n0}} + \bar{C}_{\text{tr}} \frac{[T]}{[A] + [S]} \quad (1a)$$

where $\bar{C}_{\text{tr}} = \bar{k}_{\text{tr}}/\bar{k}_{\text{p}}$. A, S, and T are defined in Scheme 6.

By making use of a long chain approximation the following expressions (eq 1b,c), relating \bar{C}_{tr} to values of the reactivity ratios and the individual transfer constants for a particular monomer ratio, can be derived.^{56,57}

$$\bar{C}_{\text{tr}} = AC_a \frac{[A] + [S]}{[A] + r_a[S]} + SC_s \frac{[A] + [S]}{r_s[A] + [S]} \quad (1b)$$

$$\bar{C}_{\text{tr}} = \frac{AC_a r_a + SC_s r_s}{A^2 r_a + 2AS + S^2 r_s} \quad (1c)$$

where A is the mole fraction of monomer A. It can be seen that \bar{C}_{tr} is a complex function of the reactivity ratios and individual transfer constants.

The transfer constant for $\text{Co}^{\text{II}}(\text{DMG-BF}_2)_2$ toward the AMS propagating radical were estimated from the slopes of the Mayo plots shown in Figure 2 for the styrene-AMS copolymerizations at 125 °C by solving eq 1a. In this analysis, $1/\bar{X}_n$ for the copolymers was approximated as $104/\bar{M}_n$. The transfer constant of $\text{Co}^{\text{II}}(\text{DMG-BF}_2)_2$ in styrene polymerization was taken to be 2700 (see above). The values of the reactivity ratios for styrene-AMS copolymerization used are shown in Table

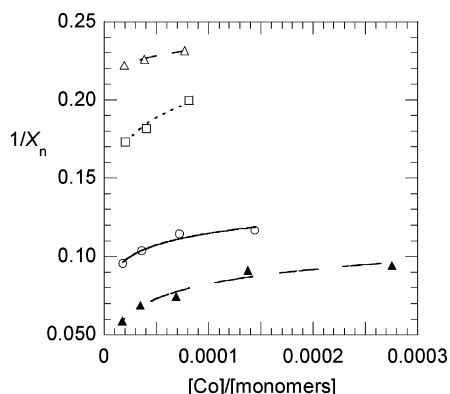


Figure 5. “Mayo” plot (reciprocal degree of polymerization (\bar{X}_n) vs [catalyst]/([total monomers]) for BA–AMS copolymerization in the presence of $^i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 80 °C with [BA]:[AMS]: (a) ~5:1 (\blacktriangle , - -), (b) ~10:1 (\circ , -), (b) ~25:1 (\square , - -), and (c) ~50:1 (\triangle , - -). Experimental conditions are summarized in Table 7.

11. This analysis suggests a transfer constant for $\text{Co}^{\text{II}}(\text{DMG-BF}_2)_2$ toward the AMS propagating radical in styrene–AMS copolymerization at 125 °C of $\sim 80000 \pm 5000$. This transfer constant, while very high, is substantially lower than that reported to apply at lower temperatures (see Table 10).³⁸ A similar determination of the transfer constant at 80 °C was not possible because of significant curvature in the Mayo plot. The reasons for curvature are discussed further below.

Molecular weight control and macromonomer purity obtained in copolymerizations of BA in the presence of $^i\text{PrCo}^{\text{III}}(\text{DMG-BF}_2)_2$ were strongly dependent on the comonomer–AMS (Table 6), MMA (Table 7), or MAN (Table 8). Macromonomer purity is significantly higher with AMS as comonomer. In copolymerizations of BA with AMS, macromonomer purity is higher for lower reaction temperatures. The overall copolymer composition is also strongly temperature dependent which is attributable to the temperature dependence of the reactivity ratios. For BA–MMA copolymerization the temperature sensitivity of copolymer composition and end group composition was within experimental error (Table 7). AMS appears to be the most effective α -methylvinyl comonomer of those used since it provides relatively high macromonomer purities for very low AMS concentrations (2 mol % relative to BA).

Analysis of the BA copolymerization data by way of a “Mayo analysis” revealed a marked deviation from a linear trend of $1/\bar{X}_n$ with \bar{M}_n for high cobalt concentrations. The effect is most marked for BA–AMS copolymerization (Figure 5) though similar trends are seen in BA–MMA (Figure 6) and BA–MAN copolymerizations. There appears to be a “saturation effect” such that above a certain cobalt concentration, the effect on \bar{M}_n of further increasing cobalt concentration is dramatically reduced. This effect is attributed to the two propagating species (that ending in BA and that ending in α -methylvinyl monomer) having markedly different reactivities toward the chain transfer catalyst. Transfer constants in polymerizations of α -methylvinyl monomers are much higher than those for monosubstituted monomers (Table 10), and this is confirmed in the present work.

The molecular weights in BA/AMS copolymerizations are dramatically influenced by the level of the α -methylvinyl monomer (see Figure 7). For high catalyst concentrations, it appears that the molecular weight is not controlled by the catalyst level but rather by the

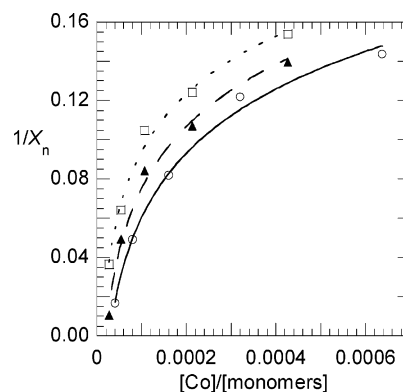


Figure 6. “Mayo” plot (reciprocal degree of polymerization (\bar{X}_n) vs [catalyst]/([total monomers]) for BA–MMA copolymerization in the presence of $^i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ for [BA]:[MMA] ~10:1 at (a) 60 °C (\circ , -), (b) 80 °C (\blacktriangle , - -), and (c) 125 °C (\square , - -). Experimental conditions are summarized in Table 5.

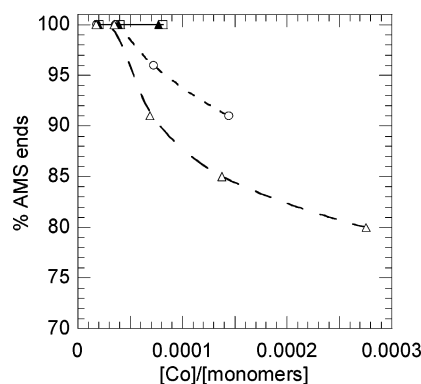


Figure 7. Fraction of AMS-derived chain ends $100 \cdot [2]/([2] + [5])$ observed in low conversion BA–AMS copolymerization in the presence of $^i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 80 °C with [BA]:[AMS]: (a) 5:1 (\blacktriangle , - -), (b) 10:1 (\square , -), (b) 25:1 (\circ , - -), and (c) 50:1 (\triangle , - -). Experimental conditions are summarized in Table 7.

ratio of the two monomers ($[S]:[A]$) in the feed. This effect is discussed further below. End group purity is, nonetheless, affected by cobalt concentration. Higher cobalt concentrations generally lead to a lower fraction of the desired macromonomer chain ends **2**—see for example Figure 7.

The effect of cobalt complex type on end group purity was also briefly explored in styrene–AMS copolymerization (Table 5)²⁹ and BA–AMS copolymerization (Tables 6 and 9). A higher fraction of the desired macromonomer chain ends **2** (i.e. higher $[2]:[5]$) was found when $\text{MeCo}^{\text{III}}(\text{DEG-BF}_2)_2$ or $\text{Co}^{\text{II}}(\text{DPG-BF}_2)_2$ was used. In the case of styrene–AMS (~10:1) copolymerization with the amount of the undesired product **5** can be more than halved (Table 5). In the case of BA–AMS copolymerization with the latter two complexes, macromonomer purities are improved to the extent that only chain ends **2** were detectable for BA–AMS ~ 50:1 (Table 9).

BA–AMS copolymerization was substantially retarded with $\text{Co}^{\text{II}}(\text{DPG-BF}_2)_2$ at 125 °C even with very low concentrations of the complex (Table 9). No similar retardation was observed with $\text{MeCo}^{\text{III}}(\text{DEG-BF}_2)_2$ or $^i\text{PrCo}^{\text{III}}(\text{DMG-BF}_2)_2$. In BA–MMA and BA–MAN copolymerization with $^i\text{PrCo}^{\text{III}}(\text{DMG-BF}_2)_2$ at >80 °C, conversions are largely independent of the cobalt concentration.

Molecular weight reductions obtained with all three complexes were similar. This suggests that the im-

Scheme 7

old chain end	+	reactant	dyad	+	new chain end
A•	+	A	$\xrightarrow{k_{aa}}$ (AA)	+	A•
A•	+	S	$\xrightarrow{k_{as}}$ (AS)	+	S•
S•	+	A	$\xrightarrow{k_{sa}}$ (SA)	+	A•
S•	+	S	$\xrightarrow{k_{ss}}$ (SS)	+	S•
A•	+	T	$\xrightarrow{k_{at}}$ (AT)	+	T•
S•	+	T	$\xrightarrow{k_{st}}$ (ST)	+	T•
T•	+	A	$\xrightarrow{k_{ta}}$ (TA)	+	A•
T•	+	S	$\xrightarrow{k_{ts}}$ (TS)	+	S•

proved specificity referred to above is due to a lower transfer constant to the monosubstituted monomer with $\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$ or $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$ rather than a higher transfer constant to AMS. However, further work is required to more rigorously establish values for the transfer constants. We have previously observed that for MMA polymerization in solution $\text{PrCo}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$ and $\text{MeCo}^{\text{III}}(\text{DEG}-\text{BF}_2)_2$ have similar transfer constants while that for $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$ is lower.⁹ Other work also suggests that the transfer constant in MMA polymerization with $\text{Co}^{\text{II}}(\text{DPG}-\text{BF}_2)_2$ is lower than that with $\text{Co}^{\text{II}}(\text{DMG}-\text{BF}_2)_2$.

Kinetic Model for Binary Copolymerization in the Presence of a Transfer Agent. In earlier work, we have shown that kinetic simulation using Monte Carlo methods⁵⁸ or numerical integration⁵⁹ can be used to predict the molecular weight, composition, and end group functionality of multicomponent copolymers formed by free radical polymerization in the presence of chain transfer agents. These methods also enabled calculation of the end group composition and molecular weight distribution based on knowledge of the reactivity ratios, and transfer constants and relative initiation rates. Given a long kinetic chain length, no absolute rate data (e.g. propagation rate constants or radical concentrations) are required to evaluate these parameters.

Even though analytical expressions have been proposed previously to predict the end group composition of binary copolymers formed in the presence of transfer agents,^{38,40,60} when applied to the systems described herein, the predictions appear inconsistent with the results of kinetic simulation^{58,59} and, more importantly, with the experimental findings reported herein. The equations substantially overestimate the fraction of end groups formed from the monomer with the lower propagation rate constant. The problem with the previous treatment^{38,40,60} lies with the use of a simplified steady-state assumption and a long chain assumption both of which are inappropriate in the present context.

The reactions that comprise terminal model copolymerization of two monomers (designated A and S) in the presence of transfer agent (T) are summarized schematically in (Scheme 7). If the kinetic chain length is long, initiation (by initiator-derived radicals) and termination reactions (by radical–radical reaction) do not

affect the copolymer composition and can be safely neglected.

On reaction with T, one chain is terminated (and an AT dyad is formed) and a new chain is started (to produce a TA dyad). The fraction of transfer agent-derived chain ends with a penultimate unit of monomer A (F_A) can be expressed as follows (eq 2):

$$F_A = \frac{P(\text{AT})}{P(\text{AT}) + P(\text{ST})} = \frac{P(\text{A})P(\text{A}|\text{T})}{P(\text{A})P(\text{A}|\text{T}) + P(\text{S})P(\text{S}|\text{T})} \quad (2)$$

where $P(\text{A})$ is the probability of finding monomer A in the chain and $P(\text{A}|\text{T})$ is the probability that a chain ending in A will react with transfer agent. $P(\text{S})$ and $P(\text{S}|\text{T})$ are defined analogously.

$P(\text{A}|\text{T})$ can be expressed as the rate of formation of end groups (AT) divided by the sum of the rates of all reactions of the propagating species A• (eq 3).

$$P(\text{A}|\text{T}) = \frac{k_{at}[\text{A}^\bullet][\text{T}]}{k_{at}[\text{A}^\bullet][\text{S}] + k_{aa}[\text{A}^\bullet][\text{A}] + k_{at}[\text{A}^\bullet][\text{T}]} \quad (3)$$

Dividing through by $k_{aa}[\text{A}^\bullet]$ gives eq 4.⁵⁸

$$P(\text{A}|\text{T}) = \frac{C_a[\text{T}]}{[\text{S}]/r_{as} + [\text{A}] + C_a[\text{T}]} \quad (4)$$

Equations 5 and 6 are derived in the same manner.

$$P(\text{A}|\text{A}) = \frac{[\text{A}]}{[\text{S}]/r_{as} + [\text{A}] + C_a[\text{T}]} \quad (5)$$

$$P(\text{A}|\text{S}) = \frac{[\text{S}]/r_{as}}{[\text{S}]/r_{as} + [\text{A}] + C_a[\text{T}]} \quad (6)$$

where r_x are the reactivity ratios ($r_x = k_{xx}/k_{xy}$) and C_x are the transfer constants ($C_x = k_{xt}/k_{xx}$).

Similar expressions for $P(\text{S}|\text{T})$, $P(\text{S}|\text{A})$ and $P(\text{S}|\text{S})$ can be derived.

Note that the transfer agent-derived species (T•) does not react with transfer agent (or does so in a degenerate process). Thus, $P(\text{T}|\text{T}) = 0$ and

$$P(\text{T}|\text{A}) = \frac{k_{ta}[\text{T}^\bullet][\text{A}]}{k_{ts}[\text{T}^\bullet][\text{S}] + k_{ta}[\text{T}^\bullet][\text{A}]} \quad (7)$$

$$= \frac{[\text{A}]}{[\text{S}]/R_t + [\text{A}]} \quad (8)$$

Similarly,

$$P(\text{T}|\text{S}) = \frac{[\text{S}]}{[\text{A}]/R_t + [\text{S}]} \quad (9)$$

where R_t reflects the specificity of the transfer agent-derived radical (T•) for the two monomers ($R_t = k_{ta}/k_{ts}$).

Since T• does not react with T an expression for $P(\text{A})$: $P(\text{S}):P(\text{T})$ can be derived that is analogous to that derived by Alfrey and Goldfinger⁶¹ to describe ternary copolymerization where one monomer (in our case, the transfer agent, T) cannot homopolymerize. Thus

$$P(A) \propto pa = [A] \left\{ \frac{R_t[A]}{r_s} + \frac{[S]}{r_s} + \frac{R_t[T]}{1/C_s} \right\} \left\{ [A] + \frac{[S]}{r_a} + \frac{[T]}{1/C_a} \right\} \quad (10)$$

$$P(S) \propto ps = [S] \left\{ \frac{R_t[A]}{r_a} + \frac{[S]}{r_a} + \frac{[T]}{1/C_a} \right\} \left\{ [S] + \frac{[A]}{r_s} + \frac{[T]}{1/C_s} \right\} \quad (11)$$

$$P(T) \propto pt = [T] \left\{ \frac{[A]}{r_s/C_a} + \frac{[S]}{r_a/C_s} + \frac{[T]}{1/C_a C_s} \right\} \{r_t[A] + [S]\} \quad (12)$$

and

$$P(A) = \frac{pa}{pa + ps + pt} \quad (13)$$

Therefore, given values for the reactivity ratios and transfer constants, it is possible to apply eq 2 to calculate the fraction of chain transfer agent-derived end groups.

The degree of polymerization is approximately equal to the reciprocal of $P(T)$.

$$\bar{X}_n \approx \frac{1}{P(T)} \quad (14)$$

Since a one unit chain would be monomer, the application of eq 2 or 14 to polymerization in systems with catalytic chain requires the contribution of 1 unit chain to be deducted. Since

$$F_A = F_A(1)P(1) + F_A(>1)P(>1) \quad (15)$$

where $F_A(n)$ is the fraction of n unit chains terminated with monomer A and $P(n)$ is the probability of forming a chain of length n .

Noting that $P(>1) = 1 - P(1)$, then

$$F_A(>1) = \frac{F_A - F_A(1)P(1)}{1 - P(1)} \quad (16)$$

where

$$F_A(1) = P(T|A) P(A|T)/P(1) \quad (17)$$

$$P(1) = P(T|A) P(A|T) + P(T|S) P(S|T) \quad (18)$$

Similarly, since the degree of polymerization, $\bar{X}_n = \bar{X}_n(>1)P(>1) + P(1)$

$$\bar{X}_n(>1) = \frac{\bar{X}_n - P(1)}{1 - P(1)} \quad (19)$$

The expressions simplify considerably if the chains formed are long since in that case $P(1) \rightarrow 0$ and the above-mentioned corrections are unnecessary and the expressions for $P(A)$ and $P(S)$ can be approximated by those for binary copolymerization in the absence of a chain transfer agent.

Analytical expressions might also be derived to encompass more complex situations such as the effects of penultimate units on reactivity ratios and various side reactions as discussed below. However, the complexity of the resultant equations would severely limit their utility and the use of numerical simulation^{43,59} is recommended in this case.

Table 14. Parameters Used to Model Copolymerizations in Presence of $^i\text{Pr}-\text{Co}^{\text{III}}(\text{DMG}-\text{BF}_2)_2$

temp	monomer A	monomer S	r_a	r_s	C_a	C_s	R
60	MMA	BA	2.24	0.414	1000	45	1
80	MMA	BA	2.24	0.414	1200	65	1
125	MMA	BA	2.24	0.414	1700	90	1
80	AMS	BA	0.5	0.13	80 000	150	1
125	AMS	BA	0.5	0.18	80 000	90	1
80	AMS	S	0.24	1.06	500 000	2000	1
125	AMS	S	0.54	1.16	300 000	1500	1

In principle, one might use the kinetic model to estimate rate constants from the experimental data using a nonlinear least-squares fitting technique. Reactivity ratios for many systems are well established or can be estimated (Table 11). Transfer constants for cobalt complexes in AMS, styrene, and MMA polymerizations have been reported (Table 10). The main unknowns are the reinitiation specificity, the transfer constants to other monomers, and the equilibrium constant for association of the propagating species with the cobalt complex. In practice, this approach has not been successful when applied to obtain all unknown parameters simultaneously. Consequently, a trial and error approach has been used in estimating and establishing sensitivity to the various kinetic parameters.

Reactivity Ratios and Transfer Constants. For the monomer ratios used in our experiments (low AMS), it is not appropriate to evaluate reactivity ratios by analysis of the composition data directly. For example, in BA–AMS copolymerization with low AMS, the overall copolymer composition is very sensitive to r_{BA} but relatively insensitive to r_{AMS} . The end group composition and the molecular weight are, however, sensitive to value of r_{AMS} .

Reactivity ratios for copolymerizations of BA and styrene with various α -methylvinyl monomers are summarized in Table 11. The literature indicates that the composition (but not the kinetics) of MMA–BA⁶² and MMA–styrene^{63–66} copolymers formed by radical polymerization are adequately described by terminal model reactivity ratios. Reported reactivity ratios for AMS–styrene⁶⁷ and AMS–BA^{68,69} show significant temperature dependence which is attributed to the reversibility of propagation. Reactivity ratios for copolymerizations of BA with MAN have not been reported. Estimates based on the use of the $Q-e$ scheme⁷⁰ and the patterns of reactivity scheme⁷¹ are shown in Table 11.

For AMS–styrene copolymerization, reactivity ratios based on the Arrhenius parameters reported by Fischer⁶⁷ have been used in our modeling (Table 14). These values allow prediction of the observed copolymer composition and values of the transfer constants can be chosen which describe of the end group composition and the molecular weight.

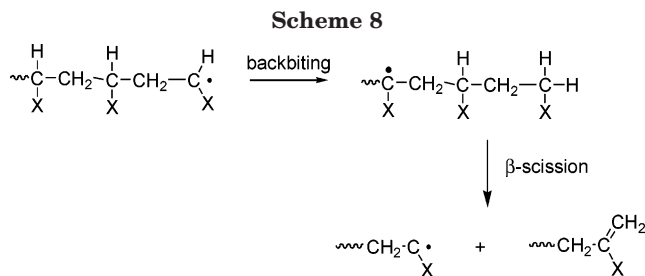
When our analysis was initiated, the only reported reactivity ratio data for the AMS–BA system was that of McManus et al.⁶⁸ Their work indicated a very low value for r_{AMS} particularly at high temperatures (Table 11). If r_{AMS} is low, then higher values of the transfer constants can be chosen to predict the observed chain end composition and molecular weight. However, these reactivity ratios were apparent reactivity ratios based on the use of a terminal model which did not allow for depropagation and are therefore perhaps not appropriate for use in the present circumstances. In our experiments, the extent of depropagation is reduced because

the propagating radical with a terminal AMS unit can be trapped by chain transfer. Application of the empirical $Q-e$ ^{70,72} or patterns⁷¹ schemes suggested a r_{BA} similar to that reported⁶⁸ but a markedly higher value for r_{AMS} (Table 11). Notwithstanding the abovementioned limitations of our data with respect to reactivity ratio estimation, fitting our experimental data for 80 °C also suggested higher values of r_{AMS} closer to those predicted by the $Q-e$ scheme. Very recently the Penlidis group⁶⁹ has reported reactivity ratios and their temperature dependence for AMS–BA copolymerization that were estimated using the Kruger⁷³ model (Table 11). The Kruger⁷³ model takes into account all possible depropagation reactions. These values are entirely consistent with our experimental observations and have been used in the present work.

Literature transfer constants for $\text{Co}^{\text{II}}(\text{DMG}-\text{BF}_2)_2$ observed in polymerizations of various (meth)acrylate esters, styrene and AMS are collected in Table 10. It has been suggested that chain transfer to the methacrylate esters may be a diffusion-controlled process.⁷⁴ In the case of styrene and monosubstituted monomers, chain transfer constants are lower, not only because the reaction of the propagating species with cobalt is slower but also because the complex reacts reversibly with propagating radicals by the process of Scheme 5 (where R^\bullet is a propagating radical) to form the corresponding alkylcobalt(III) complex, thus rendering some fraction of the cobalt complex in a dormant state.^{28,53,54,75} Some data also suggest that the transfer constant to MMA may be chain length dependent for chain lengths <7 units.⁷⁶

While there have been a few studies of hydrogen atom transfer to monomers from cobalt hydrides,^{77,78} there are as yet no reliable data for relative rates of initiation (R_i) by this species for the present systems. On the basis of an analysis of the dimeric products formed in styrene–MMA copolymerization in the presence of $\text{Co}^{\text{II}}(\text{DMG})_2$, Gruel and Harwood³⁴ suggested that there is a preference for hydrogen atom transfer to styrene over MMA. Analysis of the dimeric products formed in copolymerizations⁷⁹ of AMS and MMA (or ethyl methacrylate) and of AMS with MAN in the presence of $\text{Bz}(\text{py})\text{Co}^{\text{III}}(\text{DMG})_2$ suggests that MMA chain ends are formed in preference to AMS or MAN. Some caution is required in interpreting these results. In both sets of experiments very high cobalt concentrations were used (0.0005–0.001 M) such that the observed product was mainly dimer. It is likely that the major (nonobserved) product was monomer, since, under these conditions, a large fraction of the initially formed monomeric radicals are also likely to be trapped by the transfer agent. The very much higher reactivity of propagating species with a terminal MMA vs styrene or AMS vs MMA means that a large fraction of those species are trapped. Thus, the dimer distribution will not reflect the relative rate of reaction of the cobalt hydride with the monomers.

From our modeling, it is clear that the end group composition and molecular weight of the product (after correction for the formation of 1 unit chains) is insensitive to the value of R_t . The reason is that, under our conditions, irrespective of the value of R_t , essentially all initiation is by way of monomer S. Initiating species formed by transfer of hydrogen to monomer A do not propagate but are immediately trapped as monomer. The value of R_t has therefore been arbitrarily assigned as 1.0. We anticipate that even though the value of R_t



has no marked effect on the composition, it may affect the rate of copolymerization.

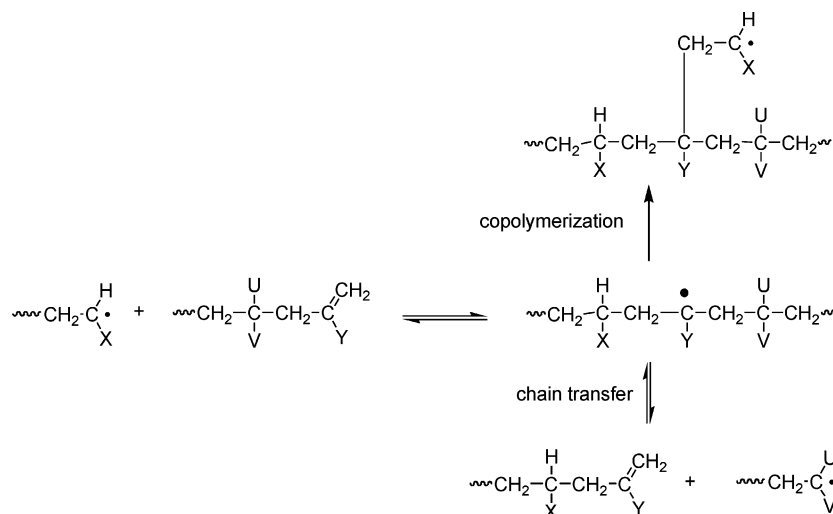
Side Reactions. Depropagation. The kinetic model described above does not allow for depropagation, and thus some caution should be exercised in their direct application to copolymerizations of AMS, particularly at high temperatures. AMS has a very low ceiling temperature and depropagation should not be ignored. Reported propagation-depropagation equilibrium constants (K) for AMS in copolymerizations with styrene and BA are shown in Table 11.⁸⁰ Predictions of end group composition may still be valid if only homodepropagation occurs since, in that case, loss of an AMS end will generate another AMS end. Furthermore, the probability of forming an AMS–AMS dyad under the conditions used (low AMS concentration) studied is very low. However, if cross depropagation occurs these expressions will tend to overestimate end group purity. Fischer⁶⁷ has indicated that cross depropagation in styrene–AMS copolymerization may become significant at temperatures >110 °C. No data are available for BA–AMS copolymerization, though it is anticipated on the basis of relative bond strengths that the cross depropagation should be less favorable in this system than for styrene–AMS copolymerization.

Transfer to AMS. Reported rate constants for transfer to monomer are more than 2 orders of magnitude higher for AMS (ca. $4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) than for other monomers (ca. $10^{-5} \text{ M}^{-1} \text{ s}^{-1}$) used in this study,⁸¹ and it has recently been reported that copolymerization of AMS with, for example, styrene may in itself provide a mechanism of molecular weight control and a method for making functional polymers.⁸² However, the concentration of AMS required to give low molecular weight polymers is very high. Given the relatively low concentrations of AMS used in the present experiments (always <10 wt %), transfer to monomer should be of little significance.

Backbiting—Fragmentation. Another side reaction that should be considered in polymerization of monosubstituted monomers is the formation of a macromonomer chain ends by backbiting/ β -scission (Scheme 8).^{29,43,83,84} It is believed that this side reaction is the main factor limiting molecular weight in high temperature polymerization or copolymerization of acrylate esters. The reaction may also occur during styrene polymerization but it is substantially less significant.^{29,83} Backbiting/ β -scission produces a polymer with macromonomer chain end (similar to **2**) but derived from the monosubstituted monomer as shown in Scheme 8.

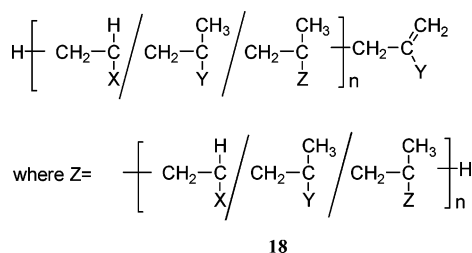
For cases where the substituents Y (on the α -methacrylate monomer) and X (on the monosubstituted monomer) are different, the formation of macromonomer chain ends by backbiting β -scission will be evident in the ^1H NMR spectrum. Thus, the ^1H NMR spectra of high conversion copolymers of BA and AMS produced in the presence of a chain transfer catalyst shows

Scheme 9



evidence of both $-\text{CH}_2-\text{C}(\text{Ph})=\text{CH}_2$ and $-\text{CH}_2-\text{C}(\text{CO}_2\text{Bu})=\text{CH}_2$ chain ends. For cases where Y and X are the same, the fraction of chains formed by backbiting β -scission should be independent of the concentration of the cobaloxime chain transfer catalyst. Thus, an upper limit for the fraction of chain ends formed by this mechanism is the ratio of molecular weights seen in the absence and presence of the chain transfer catalyst. For the experiments reported in this paper where conversions are low, the conditions are such that the formation of chain ends by backbiting-fragmentation is negligible.

Macromonomer Copolymerization. The initially formed macromonomers are likely to be reactive under the polymerization conditions, particularly at high monomer conversions. The radical formed by addition to the macromonomer may undergo β -scission (to return to starting materials or to give chain transfer) or it may propagate leading to branch formation (Scheme 9). This latter pathway may be desirable in some circumstances since it provides a route to hyperbranched polymers based on acrylate monomers.⁸⁵ Macromonomer products with end group **2**, rather than being shown as (**9a–12a** or **9c–12c**), should be represented by structure **18**. The nonmacromonomer products with end group **5** (**9b–12b** or **9d–12d**) can be similarly described. The fraction of the repeat unit $\text{CH}_2-\text{C}(\text{CH}_3)\text{Z}$ in **18** (i.e. the extent of branching) should be reduced by increasing temperature, by increasing dilution and is favored by low monomer conversions.^{8,9}



Graft formation will also complicate product analysis of high conversion polymerizations. A recent study on bulk BA–MMA copolymerization with $\text{Co}^{\text{II}}(\text{DMG}-\text{BF}_2)_2$ at 60 °C indicates that graft formation by copolymerization of macromonomer is significant at high conversions.⁴³ Yamada et al.⁸⁶ have reported that MA and styrene macromonomers give exclusively copolymeriza-

tion at 60 °C when polymerized with the respective monomers.

The polymerizations reported herein were carried out in solution, were generally carried out at high reaction temperatures (120 °C) and were only taken to low conversion such that the molar concentration of macromonomer is very low. The measured transfer constants of styrene macromonomers with terminal AMS chain ends in polymerizations of styrene are 0.11–0.15 at 120 °C as compared to (~ 0) at 80 °C (Table 12). These results are consistent with cross propagation being favored over fragmentation at the lower temperature (80 °C) and with fragmentation being a preferred pathway at the higher temperature (120 °C) such that graft copolymer formation becomes less important. Chain transfer to formed macromonomer by addition fragmentation (RAFT) does not give rise to byproduct formation. It also provides a mechanism for chain equilibration process as shown in Scheme 9 and may lead to lower polydispersities.⁹

Predictions of Copolymer Molecular Weight, End Groups, and Composition. Predictions of molecular weight and end group composition using our kinetic model for AMS–styrene copolymerization are shown in Figure 3 (125 °C) and Figure 4 (80 °C). The kinetic parameters used are given in Table 14. It can be seen that we are able to predict all of the generic trends observed experimentally. It would seem that the lower macromonomer purity observed for the lower reaction temperatures is largely attributable to less favorable reactivity ratios.

Predictions of molecular weight and end group composition and overall copolymer composition for BA copolymerizations are shown in Figure 8 (BA–AMS 80 °C), Figure 9 (BA–AMS 125 °C), Figure 10 (BA–MMA 60 °C) and Figure 11 (BA–MMA 125 °C), respectively. Again, all of the experimentally observed trends are predicted by the kinetic model.

The estimated transfer constant of cobalt complex to the BA propagating species is small (~ 45 –90 in MMA copolymerization ~ 150 –200 in AMS copolymerization). The apparent transfer constant to the MMA propagating species in these copolymerizations is in the range 1000–1700. This is up to 30-fold lower than observed in MMA homopolymerization (see Table 10). The apparent transfer constant to the MMA propagating species is also much lower than previously reported. A probable ex-

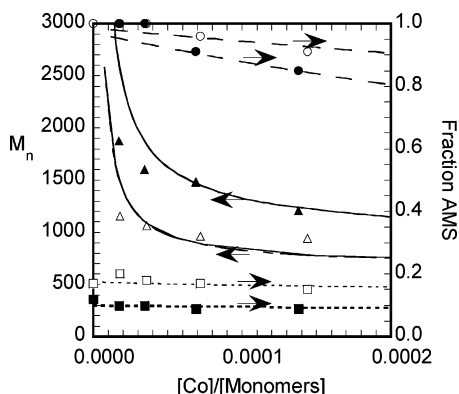


Figure 8. Comparison of observed and predicted properties of BA-AMS formed in copolymerization with [BA]:[AMS] \sim 50:1 (closed symbols) or \sim 25:1 (open symbols) in the presence of $i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 80 °C: (a) fraction of AMS-derived chain ends $[2]/([2] + [5])$ (experimental, \bullet ; predicted, $- -$), (b) predicted fraction of AMS in copolymer (experimental, \blacksquare ; predicted, $- -$), and (c) number-average molecular weight (\bar{M}_n experimental, \blacktriangle ; \bar{M}_n predicted, $- -$). Experimental conditions are summarized in Table 6. Parameters used in the fit are given in Table 14.

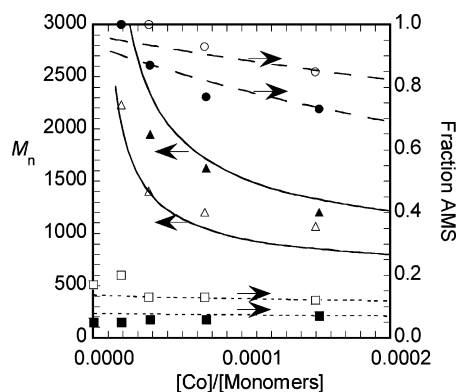


Figure 9. Comparison of observed and predicted properties of BA-AMS formed in copolymerization with [BA]:[AMS] \sim 50:1 (closed symbols) or \sim 25:1 (open symbols) in the presence of $i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 125 °C: (a) fraction of AMS-derived chain ends $[2]/([2] + [5])$ (experimental, \bullet ; predicted, $- -$), (b) predicted fraction of AMS in copolymer (experimental, \blacksquare ; predicted, $- -$), and (c) number-average molecular weight (\bar{M}_n experimental, \blacktriangle ; \bar{M}_n predicted, $- -$). Experimental conditions are summarized in Table 6. Parameters used in fit are given in Table 14.

planation is that much of the cobalt complex in the predominantly BA reaction medium is in an inactive form as the alkylcobalt(III) complex formed by reversible coupling between the BA propagating species and the active cobalt(II) complex (see above).

The predicted dependence of the molecular weight on cobalt concentration is similar to that observed experimentally. The “saturation effect” referred to above can be related to two factors:

(a) The first is the fact that the transfer constants C_s involving the propagating species **3** (with a terminal unit derived from the monosubstituted monomer) are much lower than C_a involving the propagating species **1**.

(b) The second is due to the monomer concentrations and reactivity ratios which dictate the likelihood of there being a α -methyl vinyl monomer at the chain end.

The failure of the traditional “Mayo analysis” when applied to BA copolymerizations occurs in part because the long chain approximation is not valid under the

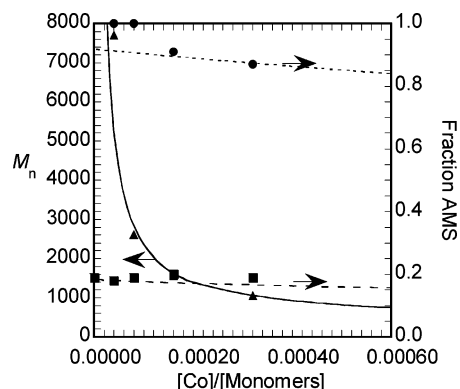


Figure 10. Comparison of observed and predicted properties of BA-MMA formed in copolymerization with [BA]:[MMA] \sim 10:1 in the presence of $i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 60 °C: (a) fraction of MMA-derived chain ends $[2]/([2] + [5])$ (experimental, \bullet ; predicted, $- -$), (b) predicted fraction of AMS in copolymer (experimental, \blacksquare ; predicted, $- -$), and (c) number-average molecular weight (\bar{M}_n experimental, \blacktriangle ; \bar{M}_n predicted, $- -$). Experimental conditions are summarized in Table 7. Parameters used in the fit are given in Table 14.

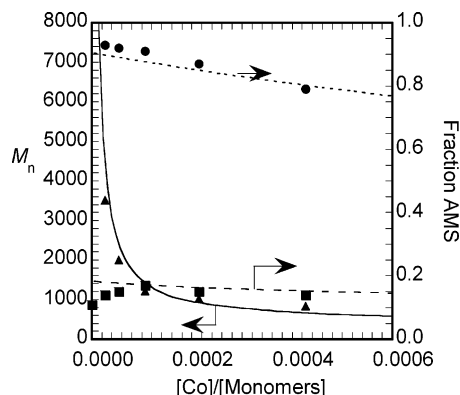


Figure 11. Comparison of observed and predicted properties of BA-MMA formed in copolymerization with [BA]:[MMA] \sim 10:1 in the presence of $i\text{Pr-Co}^{\text{III}}(\text{DMG-BF}_2)_2$ at 125 °C: (a) fraction of MMA-derived chain ends $[2]/([2] + [5])$ (experimental, \bullet ; predicted, $- -$), (b) predicted fraction of AMS in copolymer (experimental, \blacksquare ; predicted, $- -$), and (c) number-average molecular weight (\bar{M}_n experimental, \blacktriangle ; \bar{M}_n predicted, $- -$). Experimental conditions are summarized in Table 7. Parameters used in the fit are given in Table 14.

conditions of our experiments which provide relatively low molecular weight polymers. The onset of the “saturation effect” occurs when the degree of polymerization approaches the number-average sequence length for the monosubstituted monomer (S) (eq 20). The dependence of the fraction macromonomer chain ends $[2]:[5]$ on cobalt concentration can also be explained in these terms.

number-average sequence length \sim

$$\frac{1}{P(\text{S}|\text{A}) + P(\text{S}|\text{T})} \quad (20)$$

Transfer Constants of Macromonomers. The apparent transfer constant for a styrene macromonomer (**9**) prepared by AMS-styrene copolymerization was evaluated to both to provide another estimate of the macromonomer purity and to gauge the importance of macromonomer copolymerization as a side reaction.

The measured transfer constants for the styrene macromonomer (**9**) can be compared with those for a macromonomer with a similar end group prepared with

an allyl sulfide transfer agent (**16**) (refer to Scheme 4),⁵⁰ a macromonomer with a methacrylate chain end (**17**) and those for AMS dimer **6** in Table 13. The transfer constants were determined using the log CLD method as described in earlier work.^{4,87} Literature values^{79,88,89} for AMS dimer **6** are also shown in Table 13. The transfer constants of the styrene macromonomers **9** and **16** are the same within experimental error after allowing for the macromonomer purity (consistent with the ~68% of chains with end groups **2** determined by NMR analysis).

The apparent transfer constant for the styrene macromonomers in styrene polymerization increases significantly with increasing temperature; from ~0 at 80 °C to 0.11–0.16 at 120 °C—see Table 13. For the polymerizations of styrene in the presence of the styrene macromonomer (**16** or **17**) at 80 °C there was no significant variation in molecular weight of the polystyrene formed with macromonomer concentration. However, some narrowing of the molecular weight distribution may be a consequence of the extent of chain branching incorporated by macromonomer copolymerization.

In contrast, we find the transfer constant for AMS dimer (**6**) shows no marked temperature dependence in styrene polymerization over the range 60–120 °C. It has a significantly lower transfer constant in BMA polymerization than in styrene polymerization at 120 °C.

The different temperature dependence seen for AMS dimer (**6**) and the styrene macromonomers is related to the propensity of the styrene macromonomer (**9**) and (**16**) to undergo copolymerization with styrene at lower temperatures (refer to Scheme 9 for the mechanism). Chain transfer by addition–fragmentation predominates at 120 °C. AMS dimer (**6**) does not undergo copolymerization with styrene in the temperature range 60–120 °C, with fragmentation being favored over propagation over the entire temperature range. The difference in behavior is attributed to the cumyl radical being a substantially better free radical leaving group than the polystyryl propagating radical.

The transfer constants for the macromonomers (**9**, **16**, or **17**) at 120 °C in styrene polymerization are similar to those observed in BMA polymerization (Table 12) and only slightly lower than those reported for methacrylate-based macromonomers in polymerizations of methacrylate esters.^{4,5} The result suggests a possible application of these macromonomers in block copolymers synthesis at higher temperatures (>120 °C).

The results also indicate that macromonomer copolymerization should occur and may be a dominant reaction during synthesis of macromonomers (**9**) in polymerizations carried to significant monomer conversion with a reaction temperature at or below 100 °C. A similar situation is likely to apply in the case of acrylate based macromonomers.

Conclusions

Copolymerization of monosubstituted monomer in the presence of α -methylvinyl monomers and a cobalt chain transfer catalyst provides a useful route to macromonomers that are composed largely of the monosubstituted monomer.

The molecular weight is dramatically influenced by the level of the α -methylvinyl monomer. For higher catalyst concentrations, the molecular weight is not controlled by the catalyst level but rather by the ratio

of the two monomers ($[S]:[A]$) in the feed. This has important practical consequences, particularly if the primary aim is molecular weight control and end group purity is less relevant. It means that the outcome of polymerization is less affected by such factors as degradation of the catalyst with reaction time. It also means less care is required in selecting the amount/quality of catalyst. This is an important consideration given the air sensitivity of certain catalysts and the very small quantities involved.

It is now possible to summarize the features important in the α -methylvinyl monomer that provide for high macromonomer purity as follows:

(a) A low reactivity ratio r_s should exist, such that the propagating radical **3** prefers to undergo cross propagation (add to the α -methyl vinyl monomer).

(b) The transfer constant C_a should be high and preferably much greater than the transfer constant C_s associated with the monosubstituted monomer.

(c) The reactivity ratio r_a is less crucial. It may be considered desirable that the radical derived from monomer A does not undergo propagation since this maximizes the likelihood that the macromonomer contains the α -methylvinyl monomer only at the chain end.

When the α -methylvinyl monomer contains appropriate functionality the chemistry described provides a route to end-functional macromonomers. Thus, hydroxy end functional polymers have been prepared using hydroxyethyl methacrylate as comonomer and isocyanato-functional polymers have been prepared using α,α -dimethyl-*m*-isopropenylbenzyl isocyanate as comonomer.^{29,30}

Note Added after ASAP Publication. This article was released ASAP on October 4, 2005. References 4, 57, 80, 83, and 94 have been revised. The correct version was posted on October 12, 2005.

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