Catalytic Chain Transfer for Molecular Weight Control in the Emulsion Polymerization of Methyl Methacrylate and Methyl Methacrylate−Styrene

K. G. Suddaby, D. M. Haddleton,* J. J. Hastings, S. N. Richards,† and J. P. O'Donnell†

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK, and Zeneca Resins, Runcorn Technical Centre, P.O. Box 8, The Heath, Runcorn, Cheshire WA7 4QD, UK

Received April 9, 1996; Revised Manuscript Received September 16, 1996⊗

ABSTRACT: The application of catalytic chain transfer in the emulsion homopolymerization of methyl methacrylate and copolymerization of methyl methacrylate and styrene has been examined. [Bis[μ-[(2,3-butanedione dioximato)(2−)-*O*:*O*′]] tetrafluorodiborato(2−)-*N*, *N*′,*N*″,*N*‴]cobalt (COBF, **1**) has been used as a low-spin cobalt(II) catalytic chain transfer agent. The number-average molecular weight of poly(methyl methacrylate) is decreased from over 120 000 in the absence of catalytic chain transfer agent to less than 3000 on addition of 36 ppm of **1** remaining constant throughout the reaction while the polydispersity index was maintained at approximately equal to 2. The mechanism is essentially the same as in solution or bulk with very small amounts of primary radical initiation, undetectable by matrix-assisted laser desorption ionization time of flight mass spectrometry, and vinyl unsaturation at the terminal end of each polymer molecule. Copolymerization of methyl methacrylate with styrene has also been demonstrated. Catalytic chain transfer polymerization has been shown to be an extremely effective method of controlling molecular weight under emulsion conditions. The effects of catalytic chain transfer agent level, feed conditions, and styrene level are presented. The behavior of catalytic chain transfer in emulsion proves to be more complicated than in solution, due to partitioning of the catalytic chain transfer agent in the compartmentalized system. COBF partitions almost equally between the organic and aqueous phases. The feed profile of each reaction ingredient is important, with the best results being obtained when catalyst is fed continually as a solution in the monomer feed. A critical level of catalyst is apparent which is shown to be related to the number of catalyst molecules per particle.

Introduction

Catalytic chain transfer polymerization (CCTP) has emerged as a method for controlling molecular weight in the radical polymerization of methacrylic monomers. The work presented in the literature to date on CCTP has dealt almost exclusively with polymerization in either bulk or solution. Low levels of catalytic chain transfer agent (CCTA), [monomer]:[CCTA] > 250 000:1, can achieve poly(alkyl methacrylate)s with molecular weights below 1000[1] when used in conjunction with conventional levels of azo thermal initiator. Other methods used to achieve such drastic molecular weight reductions suffer distinct disadvantages such as (1) high temperatures requiring high boiling solvents resulting in problems associated with subsequent residual solvent removal; (2) high levels of conventional chain transfer agents, such as thiols, (i.e. stoichiometric amounts) giving problems associated with odor, color, etc.; and (3) high levels of thermal initiator, often up to 10 wt %, with the associated expense.

Free radical polymerizations of methacrylate monomers are often conducted under heterogeneous conditions, e.g. emulsion or suspension. The use of water as a dispersion medium allows efficient removal of the heat of polymerization, reactions to be taken to very high conversion (low residual monomer), and production of polymer in a commercially useful form. Acrylic polymers from emulsion polymerization are widely used as surface coatings, adhesives, etc. As such, we have been interested in developing CCTP for use in emulsion polymerization.

Catalytic chain transfer polymerization was discovered in 1975 and first described in the Western literature in the early 1980s.[2−6] This was based on the use of cobalt porphyrins as the CCTAs. While effective as CCTAs, cobalt porphyrins suffer from the disadvantages of cost, limited solubility in polar media, and strong color; all adversely affecting commercial exploitation. A number of other cobalt(II) compounds, invariably low spin, have since been shown to be active in CCTP. Notable among these are cobaloxime and its derivatives.[1,7−11] These compounds have significant advantages over the porphyrins; they are relatively inexpensive, much less colored, more active, and possess a wide range of solubilities.

The literature dealing with CCTP has been the subject of two recent reviews.[12,13] CCTP occurs when catalytic quantities (ppm levels) of active low-spin cobalt(II) macrocycles are used to perturb radical polymerizations of methacrylates or methacrylate-containing copolymerizations. These compounds have the highest known chain transfer constants (C_s) often in excess of 40 000, i.e. approximately 40 000 times more effective than most thiols in methacrylate polymerizations. The exact mechanism of CCTP is not well-understood,[12,14] but it is believed to occur via a Co(II)/Co(III) redox couple. The important steps in the catalytic cycle are presented in Figure 1,[12] which shows the boron fluoride derivative of cobaloxime, **1** (or [bis-[μ-[(2,3-butanedione dioximato)(2−)-*O*:*O*′]] tetrafluorodiborato(2−)-*N*, *N*′, *N*″, *N*‴] cobalt), as the CCTA.

---

* Author to whom all correspondence should be addressed. Email: msrgs@csv.warwick.ac.uk. phone: 01203 523256. Fax: 01203 524112.

† Runcorn Technical Centre.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

S0024-9297(96)00528-1 CCC: $12.00

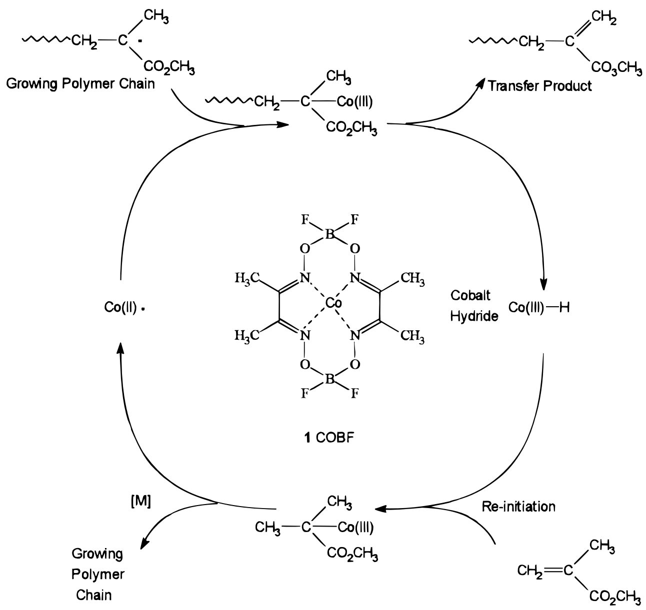
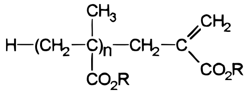


Figure 1. A simplified catalytic cycle for catalytic chain transfer polymerization.

The products from CCTP of methacrylates are α-substituted acrylate macromonomers with structure **2**.



$$H{-}(CH_2{-}\overset{CH_3}{\underset{CO_2R}{C}})_n{-}CH_2{-}C(=CH_2){-}CO_2R$$

2

Thus CCTP is an attractive method for the synthesis of low molecular weight polymers and macromonomers[15−20] since it couples the versatility of a radical system with the unique properties of the catalytic chain transfer agents. These α-substituted acrylate macromonomers can also be made to undergo a facile β-scission, making themselves useful as chain transfer agents[16−19] (by an addition−fragmentation mechanism) and as intermediates in the synthesis of telechelics, block copolymers, and other macromonomers.[21] Oligomeric and functionalized materials are increasingly important to the polymer industry since there is a drive, due to environmental legislation, toward low volatile organic content (VOC) products such as high solids coatings, radiation cured systems, and powder coatings. Likewise, macromonomers have been of considerable interest in recent years since they are important building blocks for materials such as graft copolymers. The utility of CCTP products in these applications has been recognized by the polymer industry and is reflected in the patent literature.[8−11,22−27] The majority of publications deal with the application of catalytic chain transfer in bulk or solution, but examples in the patent literature do apply CCT to emulsion and suspension.[11,22,23,28,29] These report only limited data, and full details of the experimental procedures are not revealed. Molecular weight data for the final products are given, but information on coagulation, conversion, and particle size are not provided. The use of **1** in MMA emulsion polymerization has been reported outside the patent literature, but efficient catalytic chain transfer was not achieved, suggesting that the process may be sensitive to at least some of the reaction components.[30]

In many cases it is desirable to have the CCTP products in the form of an emulsion or dispersion. At least one case exists where a monomer solution of macromonomer from catalytic chain transfer was homogenized in an aqueous phase to make an emulsion. The resultant macromonomer dispersion was then used in miniemulsion polymerization[31] to ultimately yield a block copolymer.

Studies of CCTP have focused primarily on methacrylates although cobalt macrocycles active in CCTP of methacrylates have been investigated with other monomers.[2,6,27,32,33] CCT occurs with styrene with a much lower transfer constant,[2,6,33] but the chain transfer is complicated by secondary processes which manifest themselves as a decrease in polymerization rate and by "poisoning" of the catalyst.[2,6] Janowicz discloses that molecular weight reductions result from addition of the cobaloxime derivative **1** to most acrylates, but little or no effect is seen in vinyl acetate polymerizations.[27] However, conversion data was not given with this data, making it difficult to determine the cause of the molecular weight reductions.

Many of the examples in the patent literature have applied CCTP to multicomponent copolymerizations where not all of the monomers are methacrylates. Catalytic chain transfer copolymerization of methacrylates with other monomers has received rather limited attention in the scientific literature.[2,34] Catalytic chain transfer occurs in copolymerizations of styrene with methacrylates[2,23−25,34] and when acrylates are a minor component in the polymerization system.[24,25] CCT is reduced or ceases in systems containing larger quantities of acrylates or vinyl acetate [26] and inhibition is reported.[2] Thus CCT can be applied to copolymerizations of vinyl monomers where methacrylates are at least a major component of the monomer feed.

The work described in this paper extends CCTP to the emulsion polymerization of methyl methacrylate and methyl methacrylate/styrene statistical copolymers. Cobaloxime boron fluoride (COBF, **1**) was used as the catalytic chain transfer agent. **1** has been previously demonstrated to be effective in bulk and solution polymerizations and also meets the requirements needed for a catalytic chain transfer agent to be effective in emulsion polymerization in that it has reasonable hydrolytic stability at low pH [35] and it is soluble in both the organic and aqueous phases. **1** is oxygen sensitive, which necessitates polymerization in the exclusion of oxygen but only as would be usual for free radical emulsion polymerization. The initiator used was the water soluble azo initiator 4,4′-azobis(4-cyanovaleric acid) (CVA). The use of azo initiators is important since peroxides or redox systems are usually incompatible with catalytic chain transfer agents due to poisoning of the catalyst.[36]

Materials and Methods

General. The monomers used were methyl methacrylate (stabilized with 5 ppm of Topanol, ICI Acrylics) and styrene (stabilized with 10−15 ppm of 4-*tert*-butylcatechol, Aldrich) and used as received. Aerosol OT-100 (Fisons, sodium bis(2-ethylhexyl) sulfosuccinate, AOT) was used as the surfactant, 4,4′-azobis(4-cyanovaleric acid) (75%+ remainder water, Aldrich) as the initiator, and reverse osmosis grade water was used to form the aqueous phase. **1** (assumed to be the bis methanol adduct) was prepared according to the procedure of Espenson.[37,38] In all cases the reagents were used without further purification steps other than deoxygenation. The water and monomers were deoxygenated by bubbling with a nitrogen stream for at least 2 h immediately prior to use. All manipulations were carried out using standard Schlenk line techniques with liquid transfer by syringe.

Table 1. Reaction Conditions Used for Emuslion (Co)polymerizations, Apparent Chain Transfer Constants, and Final Product Particle Size

run	[COBF]/[monomer] × 10^{6a}	monomer feed (over 60 min)	COBF feed (in monomer)	STY/MMA	apparent C_s	final product diameter (nm) (CHDF)		final product diameter (nm) (light scattering)	
						D_n	D_w	D_z	std dev
0	0	yes	yes	0				65.9	12.5
1	36	yes	yes	0	1050	102.2	118.1	138.7	20.6
2	36	yes	yes	0	940	103.6	121.3	138.4	25.9
3	27	yes	yes	0	943	95.2	107.2	129.6	18.5
4	18	yes	yes	0	508	75.7	82.6	85.0	19.8
5	36	no	no	0	934	311^b	368^b	439.4	143.1
6	36	yes	no	0	174	104.9	126.4	161.3	33.6
7	37	yes	yes	0.311	346	68.3	79.3	101.8	25.9
8	37	yes	yes	0.934	112	70.0	80.5		

[a] Based on moles of monomer. [b] Sample is multimodal.

A 1 L flange flask with a 100 mm bore, modified to have four baffles, was used as the polymerization reactor. The reaction was performed in an 80 ± 0.5 °C water bath and stirred at 150 rpm by a turbine impeller.

Polymerization. All polymerizations used a recipe comprising of 450 mL water, 200 mL monomer, 2.00 g Aerosol OT-100, and 2.00 g of CVA, giving 30% solids. The exact conditions used for each run are summarized in Table 1. This procedure produced negligible coagulum, except in run 5, which is discussed below.

The following procedure was followed for runs 1 and 2, which were typical reactions. The AOT was placed in the reactor prior to the deoxygenated water, which was then allowed to come to reaction temperature. Compound **1** (30 mg, 6.73×10^{-5} mol; 27 800:1 MMA:**1**, 36 ppm of **1** based on moles of MMA) was dissolved in deoxygenated monomer in a Schlenk tube. The CVA was added to the reactor immediately prior to starting the monomer feed. The monomer was added at 3.33 mL/min using an FMI metering pump to give a total feed time of 60 min. Temperature readings and samples were collected every 20 min for at least 2 h and the reactions left to run overnight before a final sample was collected. All samples were analyzed for conversion, molecular weight, and particle size. The percent age of solids for each sample was corrected for the surfactant and initiator to obtain monomer conversions.

Molecular weights (apparent molecular weights in the case of copolymers) were determined by size exclusion chromatography (SEC) using a Polymer Laboratories system with differential refractive index detection. The SEC eluent was THF with a flow rate of 1.00 mL $\min^{-1}$. Toluene (0.2%) was used as an internal standard and flow marker for each sample. The column set consisted of a Polymer Laboratories 5 μm guard column (50 × 7.5 mm) and two Polymer Laboratories Mixed-D columns (300 × 7.5 mm). Data were collected at 1 point per second. The system was calibrated with 10 Polymer Laboratories PMMA standards and pure MMA dimer. The calibration curve consisted of log molecular weight expressed as a third-order polynomial in elution volume.

Matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF-MS) was carried out on a Kratos Kompact III spectrometer in the reflectron mode. This instrument incorporates a 337 nm nitrogen laser with a 3 ns pulse duration and an electron multiplier detector. The sample was deposited in a 2,5-dihydroxybenzoic acid matrix from an acetone−water mixture doped with NaCl. This resulted in each species being observed as its Na^+ adduct at molecular mass M + 23. The spectrometer was calibrated internally using bovine insulin (5734) and sodium (22.9898). The width of peaks in the region of 4000 Da at half peak height is approximately 4 Da.

Partitioning of COBF. The partition coefficient for **1** between MMA and water was determined using UV/vis spectroscopy. Beer Lambert plots for COBF in MMA and water gave values of $\epsilon = 3438$ ($\lambda_{max} = 445$ nm) and 3641 ($\lambda_{max} = 454$ nm), respectively. COBF was dissolved in MMA and the mixture added to water and then shaken vigorously. The two phases were allowed to separate and a portion of each solution was placed in a 1 cm pathlength quartz cell and the absorbance determined at λ_{max} using a Perkin-Elmer λ15 spectrophotometer. The relative concentrations in the two phases were determined from these absorbances.

Particle Size. Particle sizes of the final products were measured using two different methods, capillary hydrodynamic fractionation (CHDF) for the number- and weight-average diameters and dynamic light scattering to measure the *z*-average diameter. The CHDF was performed on a Matec Applied Sciences CHDF-1100 instrument calibrated using a series of narrow polydispersity polystyrene latexes.[39,40] Particle size analysis using dynamic light scattering was conducted using a Malvern Autosizer II C instrument after high dilution of the latex samples with distilled water.

Results and Discussion

Emulsion CCTP of MMA. The utility of CCTP for molecular weight control in emulsions is immediately apparent from comparing the data for the emulsion polymerization of MMA both in the presence (of the standard level, 36 ppm, runs 1 and 2) and absence (run 0) of **1**, which are reported in Table 2. The reaction with 36 ppm of **1** produces a 40-fold decrease in the number-average molecular weight and yields polymer with a polydispersity (M_w/M_n) of approximately 2. The excellent agreement between the replicate reactions 1 and 2 demonstrates the reproducibility of CCTP in emulsions.

Analysis of the products from the emulsion polymerizations of MMA containing **1** shows that CCTP in emulsions is not only an effective method of molecular weight control but that it is also an effective means of producing macromonomer emulsions of high purity. The ^{1}H NMR spectrum of the final product from run 1 is given in Figure 2. This spectrum is consistent with that of the product expected from CCTP, **2**. Residual monomer (**2** with $n = 0$) gives vinyl peaks at 6.05 and 5.5 ppm, while macromonomer products (**2** with $n > 0$) give vinyl signals at 6.15 and 5.45 ppm, as shown in the expanded inset. Free monomer and macromonomer can thus be distinguished and the relative amounts of each can be determined by the ratio of the signals at 6.05 and 6.15 ppm. In this sample the level of free monomer was below the detection limits of the instrument. The relative integrals of the methoxy and vinyl regions give a number-average degree of polymerization of 24.9, assuming all polymer chains have a terminal unsaturation. This is in good agreement with the value of 26.0 obtained by SEC (Table 2) and therefore consistent with product having structure **2** and a high degree of purity.

The MALDI-TOF spectrum of the final product from run 1 is given in Figure 3. MALDI is a very soft ionization technique which results in little or no fragmentation. These results are also consistent with the polymer having structure **2**, although resolution is limited to 4−5 Da. A single series, the Na^+ adduct, is seen with each species having a molecular weight

Table 2. Data for MMA Homopolymerizations with 0, 36, and 36 ppm of COBF (runs 0, 1, and 2, respectively) under the Conditions Outlined in the Experimental Section[a]

run	time (min)	reaction temp (°C)	conversion		molecular weight distribution[b]			particle diameter (nm)	
			instant	total	M_n	M_w	PDI	z mean	std dev
0	0	78.4							
0	20	80.7	0.916	0.305	126842	257559	2.03		
0	40	80.9	0.970	0.647	128298	295695	2.31		
0	60	81.9	0.979	0.979	130328	343830	2.64		
0	80	78.5	0.998	0.998	138488	340746	2.46		
0	100	78.5	1.002	1.002	149620	388700	2.42		
0	120	77.7	1.002	1.002	148051	381428	2.58		
0	final		0.998	0.998	142720	366894	2.57	65.9	12.5
1	0	77.7							
1	20	79.7	0.410	0.137	3214	7632	2.38		
1	40	79.8	0.460	0.307	2070	5110	2.47		
1	60	79.8	0.518	0.518	1834	4487	2.45		
1	80	79.9	0.697	0.697	2083	4524	2.17		
1	100	80.5	0.947	0.947	2407	5171	2.15		
1	120	78.7	0.976	0.976	2535	5145	2.03		
1	final		0.985	0.985	2600	5170	1.99	138.7	20.6
2	0	78.3							
2	20	79.8	0.378	0.126	3095	8129	2.63		
2	40	80.1	0.443	0.295	1954	5084	2.60		
2	60	80.0	0.516	0.516	2007	4712	2.35		
2	80	80.3	0.765	0.765	2231	4750	2.13		
2	100	80.0	1.004	1.004	2720	5391	1.96		
2	120	77.9	0.986	0.986	2876	5522	1.92		
2	final	78.9	0.985	0.985	2889	5576	1.93	138.4	25.9

[a] The monomer containing COBF was fed over 60 min. [b] The GPC column set used to obtain molecular weight data for run 2 consisted of a guard column and a single Mixed-E column.

consistent with it being comprised solely of MMA repeat units ($n[100.12] + 23$). Of note is the absence of peaks arising from primary radical initiation, which would result in macromolecules containing an initiator fragment ($n[100.12] + 23 + 126$), indicating that polymer chains arising from primary radical initiation make a negligible contribution to the total polymer. Thus both chain initiation and termination under emulsion CCT conditions are essentially identical to those of CCT in bulk and solution. Comparisons of MALDI-TOF spectra of similar polymers with the number distributions obtained from SEC chromatograms and predicted by theoretical considerations showed that, under the conditions used, the MALDI-TOF spectra did not correspond to the number distributions of the polymer.[41] This invalidated comparisons of the relative intensities of the peaks in the MALDI-TOF spectrum with theoretical distributions.

A rough measure of the chain transfer activity for **1** in these polymerizations is the apparent chain transfer constant (C'_s) of the catalyst in the polymerizations. These values are presented in Table 1. They were obtained by using equation 1, which is a rearrangement

$$C'_s = \left(\frac{1}{\mathrm{DP}_n} - \frac{1}{\mathrm{DP}_{n,0}}\right)\frac{[\mathrm{M}]}{[\mathrm{COBF}]} \qquad (1)$$

of the Mayo equation. All number average degrees of polymerization ($\mathrm{DP_n}$) values were calculated from M_n of the final product assuming it was comprised of MMA, and number average degree of polymerization in the absence of CCTA ($\mathrm{DP_{n,0}}$) was determined from run 0, which had no catalytic chain transfer agent added. It is noted that in no way should these values of the apparent chain transfer constants be taken as true chain transfer coefficients as many of the assumptions of the Mayo equation are violated by these polymerizations. Furthermore, the chain transfer agent is catalytic, is fed in many of these polymerizations, and is distributed in all phases of these heterogeneous systems. Nonetheless, this crude measure of the chain transfer coefficient is informative. Runs 1 and 2 have apparent chain transfer constants of 1050 and 940, respectively. Although this is an order of magnitude lower than in bulk or solution, it is orders of magnitude better than the chain transfer constants of conventional chain transfer agents, indicating the effectiveness of CCT under emulsion conditions.

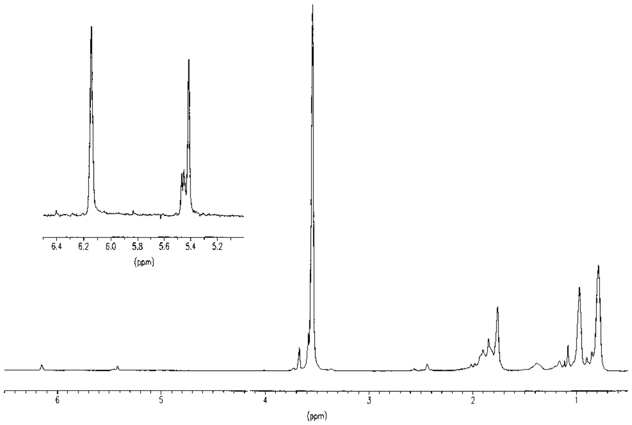


Figure 2. ^{1}H NMR spectrum of the final product from run 1 with a 32 times blow up of the vinyl region.

Effect of Level of Catalytic Chain Transfer agent in MMA Emulsion Polymerization. MMA emulsion homopolymerizations were also conducted at 27 and 18 ppm of **1**, runs 3 and 4, respectively. The data from these polymerizations can be combined with those of runs 0, 1, and 2 (0, 36, and 36 ppm of **1**) to examine the effect of varying the amount of **1** in the emulsion polymerization of MMA.

The conversion data in Figure 4 show that the rate of polymerization decreases as the level of CCTA is increased. Also, it can be seen that two very different behaviors are occurring. The polymerizations containing low CCTA levels (0 and 18 ppm, runs 0 and 4) strongly resemble each other, as do the polymerizations

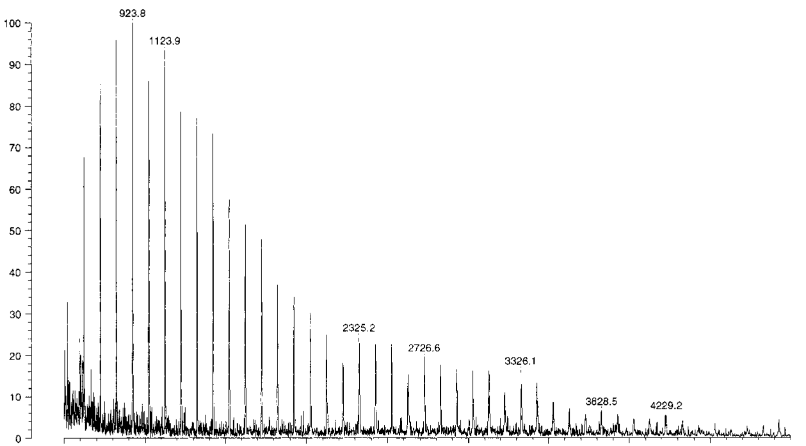


Figure 3. MALDI-TOF spectrum of the final product from run 1.

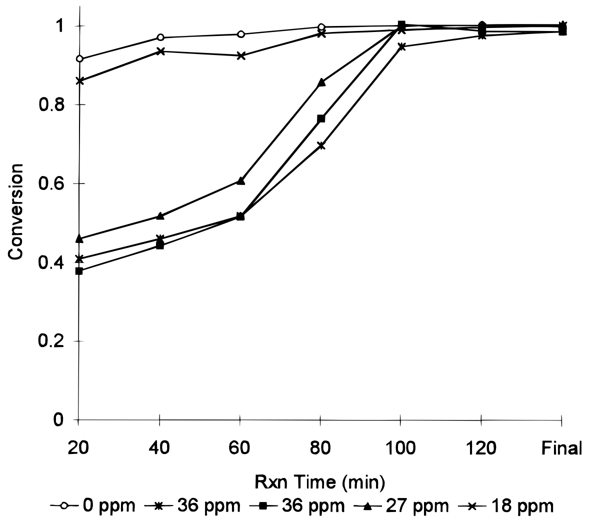


Figure 4. Instantaneous conversion as a function of time for MMA homopolymerizations with 0, 18, 27, 36, and 36 ppm of **1** (runs 0, 4, 3, 1, and 2, respectively).

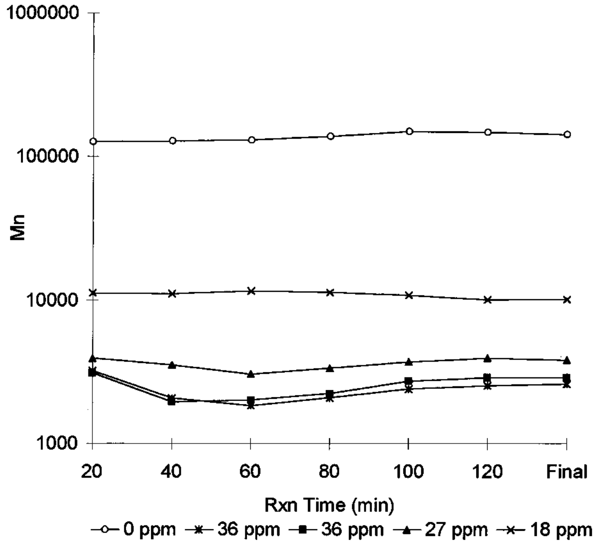


Figure 5. Number-average molecular weight as a function of time for MMA homopolymerizations with 0, 18, 27, 36, and 36 ppm of **1** (runs 0, 4, 3, 1, and 2, respectively).

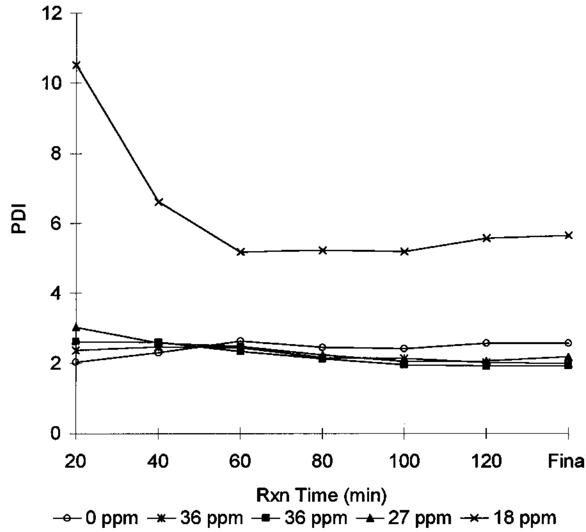


Figure 6. Polydispersity index as a function of time for MMA homopolymerizations with 0, 18, 27, 36, and 36 ppm of **1** (runs 0, 4, 3, 1, and 2, respectively).

at high CCTA levels (27 and 36 ppm, runs 1–3). Polymerizations with low amounts of CCTA operate near starved feed conditions, remaining at high conversion throughout the polymerization, while with higher amounts of **1** polymerizations are at moderate conversions until the monomer feed is stopped at 60 min. MMA emulsion polymerizations are generally pseudobulk systems (the effects of compartmentalization can be ignored)[42] and termination is rate-determining. Termination is normally diffusion-controlled and hence chain length dependent. Since the mobility of short radical chains is much higher than that of long radical chains, chain transfer will increase the rate of termination, decreasing the overall rate of polymerization. This is seen in Figure 4, where conversion decreases with CCTA concentration.

The molecular weight data for polymerizations at the different CCTA levels show that **1** has significant chain transfer activity in all cases. M_n is plotted on a logarithmic scale as a function of time in Figure 5. By examining the molecular weight data, it again becomes apparent that two different behaviors are seen in the polymerizations containing **1**. The three reactions with high concentrations of **1** (runs 1, 2, and 3 with 36, 36, and 27 ppm, respectively) all have essentially the same value of the apparent chain transfer constant, twice that of the polymerization with the lower concentration of **1** (run 4, 18 ppm). It is also worthwhile to examine the breadth of the molecular weight distributions, as measured by the polydispersity index (PDI) of the products from these emulsions. These are plotted in Figure 6.

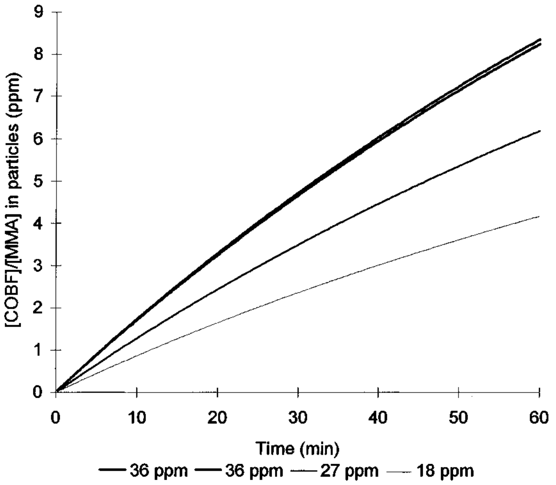
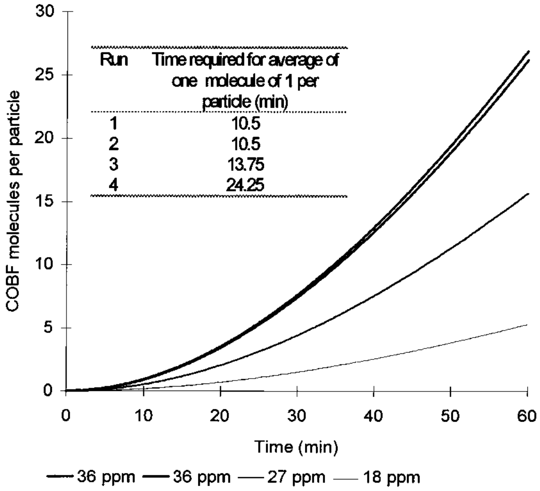


Figure 7. Average [**1**]/[MMA] in the particles as a function of time for MMA homopolymerizations with 18, 27, 36, and 36 ppm of **1** (runs 4, 3, 1, and 2, respectively).



Run	Time required for average of one molecule of 1 per particle (min)
1	10.5
2	10.5
3	13.75
4	24.25

Figure 8. Average number of **1** molecules per particle as a function of time for MMA homopolymerizations with 18, 27, 36, and 36 ppm of **1** (runs 4, 3, 1, and 2, respectively).

In general, the final products from these polymerizations have relatively narrow molecular weight distributions, having PDI between 1.9 and 2.6. However, run 4 (18 ppm of **1**) is a notable exception and does not fit in with the other data. The polymer produced in this run has a very broad molecular weight distribution, with PDIs which vary between 10.5 and 5.2. This suggests that more than one mode of polymerization (i.e. polymerization at very different concentrations of **1**) may be occurring in run 4. It will be seen that low apparent chain transfer constants are invariably associated with polymerizations having high polydispersities. It is also worth noting that the molecular weight distribution narrows as the reaction progresses in the presence of **1**, while the molecular weight distribution of the conventional emulsion polymerization broadens as the polymerization progresses.

The molecular weight data indicate that under emulsion polymerization conditions **1** acts as a very efficient catalytic chain transfer agent. However, the activity of **1**, under these emulsion conditions, is significantly lower than it is in bulk or solution. Comparing the number-average molecular weight of the products obtained at 36 ppm of **1** in emulsions with those obtained in bulk shows that similar molecular weights would be produced in bulk at a 1 ppm of **1** [1] concentration. In these emulsion polymerizations, the apparent chain transfer constants vary between 500 and 1000, which is much lower than the bulk chain transfer constant of **1** of around 40 000.[1] Hence, under emulsion conditions, all of the added CCTA cannot be active. Much of it is either inaccessible at the locus of the majority of chain growth, or is being destroyed (or poisoned). Both possibilities must be entertained.

The concentration of **1** in the organic phase is very different from that in the monomer feed since it partitions between the aqueous and organic phases and the monomer is added during the reaction. The partitioning of **1** between water and MMA at room temperature is such that $[\mathrm{COBF}]_{\mathrm{MMA}}/[\mathrm{COBF}]_{\mathrm{Aq}} = 0.68$. If it is assumed that this value holds for the partitioning between the aqueous and organic phases for these polymerizations, then the distribution of **1** can be determined. Figure 7 plots the concentration of **1** in the latex particles for runs 1−4 as a function of time. After 60 min the feed is finished and the concentration should remain approximately constant. All of the polymerizations begin with no catalytic chain transfer agent, but in the absence of any loss of catalyst, the concentration of **1** in the latex particles increases as the polymerization proceeds. With the further assumptions that all of the monomer exists in polymer particles, and that the number of particles stays constant throughout the polymerization, the average number of **1** molecules per particle can be calculated as a function of time. The number of particles was determined by dividing the total volume of monomer added by the average volume of a particle based the number-average diameter of the final product. Figure 8 shows the average number of molecules of catalytic chain transfer agent per particle during the feed for runs 1−4. Notably, all four runs have on average less than one molecule of COBF per particle during the first 10 min of polymerization. Run 4 with the lowest level of CCTA in the feed (18 ppm) has less than one molecule of **1** per latex particle for the first 24 min of polymerization.

The observed decrease of the number-average molecular weight with time during the early stages of the polymerizations in runs 1−3 is consistent with the build up of **1** within the particles during the feed stage of the polymerization. The low average number of **1** molecules per latex particle in run 4 (average at end of feed 5.32) is consistent with the high polydispersity of the polymer made in this reaction. The exact number of molecules of **1** found in a given latex particles at any given time will be distributed about the average value. Since each particle must possess a discrete number of molecules, this distribution leads to large variations in the ratio of the concentration of **1** and monomer in systems having low average numbers of CCTA molecules per particle.

Some of the decreased activity of the CCTA may also result from immobilization of the catalyst in high viscosity particles. Run 4 has the lowest apparent chain transfer constant and it operates under conditions which are close to starved feed. Part of the catalyst may be inaccessible if the particles are glassy.

A further possibility for the decreased activity of the CCTA is that the stability of the catalyst may be limited under the polymerization conditions used. Marchaj and co-workers [35] report that **1** is stable at neutral pH but is susceptible to a slow hydrolysis (rate constant of ~1 × 10^{-4} s^{-1}) at pH 1 and 25 °C. This hydrolysis was accelerated by a factor of 7 by addition of oxygen and

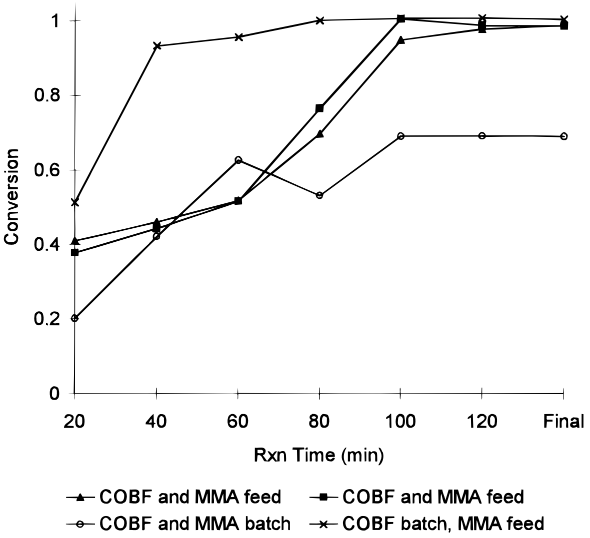


Figure 9. Instantaneous conversion as function of time for MMA homopolymerizations with 36 ppm of **1** with **1**/MMA feed, **1**/MMA batch, and **1** batch with MMA feed (runs 1 and 2, 5, and 6, respectively).

bromide. The final product from run 1 (36 ppm of **1**) was found to have a pH of 3.0, making catalyst destruction by hydrolysis likely. Presumably, the higher temperatures used in this work would make the rate of catalyst hydrolysis significant at pH 3. This would explain the increase in number-average molecular weight which occurs after 60 min (when the feed has stopped and **1** is at its maximum concentration) for runs 1−3. If CCTA was not being lost, M_n would be expected to decrease since [**1**]/[MMA] in the particles would increase as monomer was consumed.

The level of **1** also influences the particle size distribution. The particle size data for these runs (Table 1) show that the number of particles decreases as the level of catalytic chain transfer agent is increased.

Effect of Feed Conditions. Three different feed conditions were investigated at 36 ppm of **1**; the catalyst was fed with the MMA over 60 min (runs 1 and 2), the catalyst and the MMA were placed in the reactor at the start of the reaction (a batch reaction, run 5), and the catalyst was placed in the reactor at the start of the reaction, but the MMA was fed over 60 min (run 6). The batch polymerization did not produce a stable emulsion, and coagulation was observed after 60 min. This accounts for both the drop in the apparent conversion that occurs between 60 and 80 min and for the apparently low final conversion for run 5 seen in Figure 9. It is also reflected in the averages and modality of the particle size distribution. While the instantaneous conversions for the batch polymerization (run 5) at 20 and 40 min are lower than those for the polymerizations under standard feed conditions (runs 1 and 2), the total conversion, and accordingly rate of polymerization, is higher since all of the MMA had been fed in the batch polymerization. Run 6 must have a high number of **1** molecules per particle from the onset of the reaction since all of the catalyst was charged into the reaction at the start of the polymerization. Despite this, it went from being at moderate conversion at 20 min to high conversion (near starved feed conditions) at longer times. Viewed in light of the behavior observed at different catalyst levels, it behaves as if it goes from a high CCTA level at 20 min to a low CCTA level at 40 min. This is also borne out by the molecular weight data.

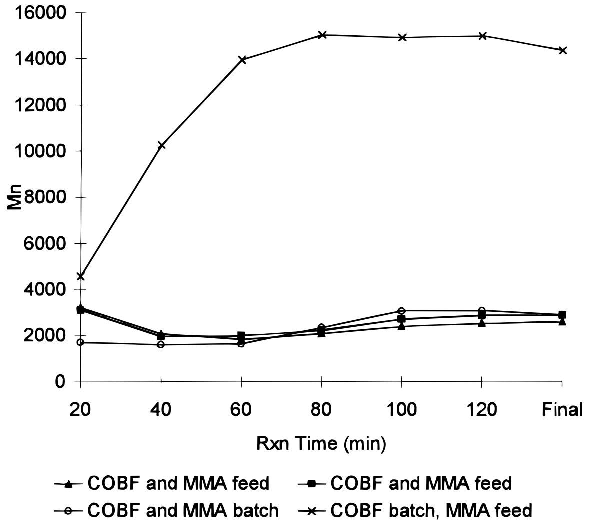


Figure 10. Number-average molecular weight as a function of time for MMA homopolymerizations with 36 ppm of **1** with **1**/MMA feed, **1**/MMA batch, and **1** batch with MMA feed (runs 1 and 2, 5, and 6, respectively).

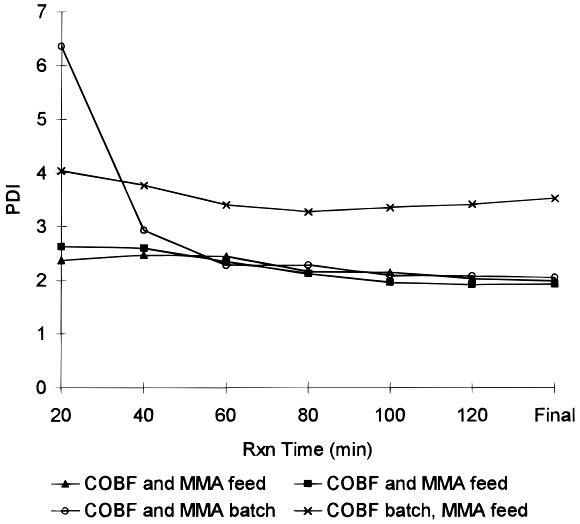


Figure 11. Polydispersity index as a function of time for MMA homopolymerizations with 36 ppm of **1**, with **1** and MMA feed, **1**/MMA batch, and **1** batch with MMA feed (runs 1 and 2, 5, and 6, respectively).

The molecular weight data in Figure 10 show run 6 (the CCTA charged into the reactor) to behave as if it had a low catalyst level. The number-average molecular weights of all samples of run 6 are higher than in the reactions where the monomer and catalyst were added together. COBF has an apparent chain transfer constant of only 174 compared to a value of about 1000 for the runs where it was added with the monomer. A dramatic increase in the number-average molecular weight also occurs as the polymerization proceeds, showing a progressive loss of catalytic activity. This indicates destruction of catalyst as the reaction progresses. The destruction of the CCTA appears to be compensated for when it is added with the monomer.

Figure 11 shows that the PDI is relatively high throughout the polymerization when the catalyst is not fed with the monomer. The combination of high M_n and polydispersity is consistent with a low number of **1** molecules per particle. Figures 10 and 11 show that the molecular weight distributions of the polymers produced by the batch reaction (run 5) and the reaction with a combined **1**/MMA feed (runs 1 and 2) are similar

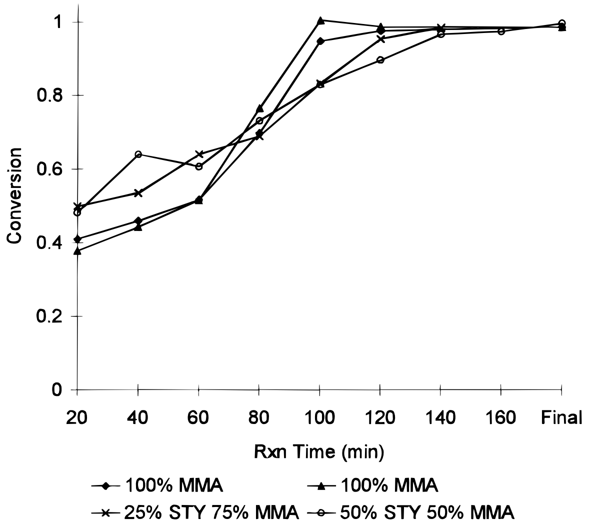


Figure 12. Instantaneous conversion as function of time for polymerizations of MMA and styrene with **1** and monomer feed with 0, 0, 25, and 50% by volume styrene feed (runs 1 and 2, 7, and 8, respectively).

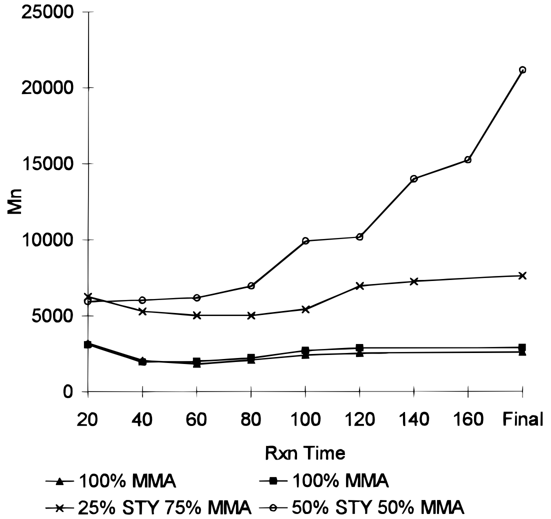


Figure 13. Number-average molecular weight as a function of time for polymerizations of MMA and styrene with **1** and monomer feed with 0, 0, 25, and 50% by volume styrene feed (runs 1 and 2, 7, and 8, respectively).

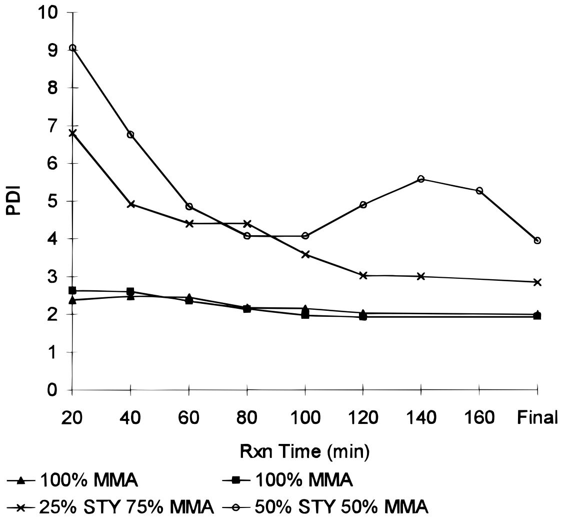


Figure 14. Polydispersity index as a function of time for polymerizations of MMA and styrene with **1** and monomer feed with 0, 0, 25, and 50% by volume styrene feed (runs 1 and 2, 7, and 8, respectively).

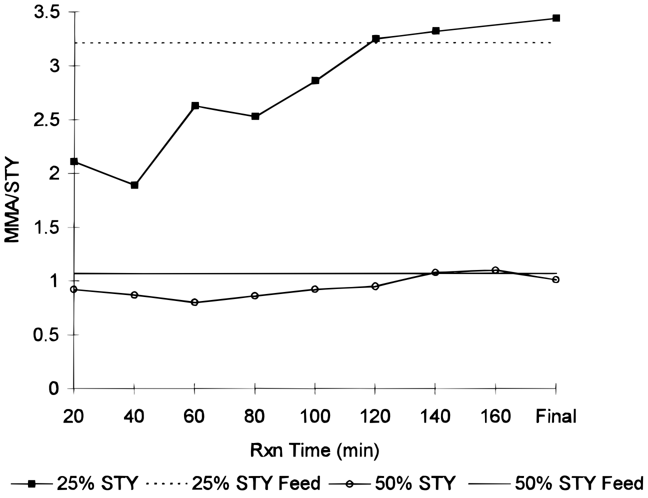


Figure 15. Copolymer composition as a function of time for polymerizations of MMA and styrene with **1** and monomer feed with 25 and 50% by volume styrene feed (runs 7 and 8, respectively).

except at short reaction times and these three reactions have similar apparent chain transfer constants. The fact that a drastic loss of catalytic activity is seen with a catalyst charge and monomer feed (run 6) but is not seen with the batch reaction (run 5) suggests that the loss occurs in the aqueous phase, consistent with hydrolysis. All of the COBF in run 6 begins in the aqueous phase but in run 5 30% of the volume is organic.

MMA/Styrene Copolymerization. Two experiments, runs 7 and 8, were conducted where 25 and 50% by volume, respectively, of the MMA was replaced by styrene. These polymerizations have approximately 3.5 times as many particles as their MMA homopolymerization analogues. Figure 12 shows that at short times these polymerizations have slightly higher instantaneous conversions than MMA homopolymerizations, but that the conversion does not increase rapidly after the feed has stopped (60 min) as it does with the MMA. Figure 13 shows that the M_n (strictly apparent M_n) increases as styrene is added to the system. This indicates that the effectiveness of **1** is reduced by styrene, as would be anticipated. The solubility of **1** in styrene is also lower than in MMA, thus its partitioning into the organic phase would be expected to be less favorable as MMA was replaced with styrene. The molecular weight of run 7 (25% styrene) remains relatively constant, as do the MMA homopolymerizations (runs 1 and 2). Conversely, the molecular weight in run 8 (50% styrene) increases continuously as the polymerization proceeds. The apparent chain transfer coefficients for the reactions containing styrene are 346 and 112. Figure 14 shows that addition of styrene appears to broaden the molecular weight distributions of the emulsion product.

The copolymer compositions in runs 7 and 8 were analyzed by ^{1}H NMR, and these data are plotted in Figure 15. In both cases the initial polymerization produces a polymer that is rich in styrene relative to the feed. The styrene and MMA were distributed though out the copolymer chains, as would be expected for statistical (random) copolymers. We do not believe that the addition of CCTAs effects the reactivity ratios in CCT copolymerization; this is the subject of current work.

The partitioning of the CCTA can be controlled by varying either catalyst or the monomer to adjust the relative solubility of the CCTA in the organic and aqueous phases. The effect of this is also under current investigation. Control of pH in these emulsions is also important, since it is believed to play a role in the loss of catalyst activity through the rate of hydrolysis of the catalytic chain transfer agent. Seeded polymerizations can be useful in eliminating some of the ambiguity associated with the compartmentalization of the organic phase by controlling the particle numbers. It should also allow better control over the average number of catalyst molecules per particle.

Conclusions

The versatility of catalytic chain transfer polymerization has been demonstrated by applying it under emulsion polymerization conditions. The catalytic chain transfer activity demonstrates that the unique level of control over both molecular weight and functionality offered by CCTP can be extended to systems where water is used as a dispersion medium. The behavior of a system in solution cannot be extrapolated to emulsion. The chain transfer catalysis is more complicated in these heterogeneous systems due to the phase behavior of the catalyst and to the compartmentalization of the organic phase. These phenomena require further attention in order to develop a satisfactory understanding of CCTP in heterogeneous systems. Control of pH in these emulsions is also important, since it is believed to play a role in the loss of catalyst activity through the rate of hydrolysis of the catalytic chain transfer agent. Seeded polymerizations can be useful in eliminating some of the ambiguity associated with the compartmentalization of the organic phase by controlling the particle numbers. It will also allow better control over the average number of catalyst molecules per particle.

Acknowledgment. The authors would like to express their gratitude to D. Kukulj, Dr. J. C. Padget, Dr. M. Heuts, and D. R. Maloney for their help with various aspects of this work. We would also like to thank EPSRC for financial support (K.G.S, ROPA:GR/K35952), and ICI Acrylics for supply of the MMA.

Supporting Information Available: Polymerization data for MMA homopolymerizations with different concentrations of **1** (runs 3 and 4 in Supplementary 1) and with 36 ppm of **1** under different feed conditions (runs 5 and 6 in Supplementary 2) and for MMA/STY copolymerizations (runs 7 and 8 in Supplementary 3); data used for determining the partition coefficient for **1** in MMA and water; Beer−Lambert plots for **1** in MMA and water; and concentrations in each phase for **1** in a mixture of MMA and water (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Amin Sanayei, R.; O'Driscoll, K. F. *J. Macromol. Sci.-Chem.* **1989**, *A26 (8)*, 1137.
(2) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1981**, *19*, 879.
(3) Smirnov, B. R.; Bel'Govskii, I. M.; Ponomarev, G. V.; Marchenko, A. P.; Enikolopyan, N. S. *Dokl. Akad. Nauk. SSSR* **1980**, *254*, 127.
(4) Smirnov, B. R.; Morozova, I. S.; Pushchaeva, L. M.; Marchenko, A. P.; Enikolopyan, N. S. *Dokl. Akad. Nauk. SSSR* **1980**, *255*, 609.
(5) Smirnov, B. R.; Morozova, I. S.; Marchenko, A. P.; Markevich, M. A.; Pushchaeva, L. M.; Enikolopyan, N. S. *Dokl. Akad. Nauk. SSSR* **1980**, *253*, 891.
(6) Smirnov, B. R.; Plotnikov, V. D.; Ozerkovskii, B. V.; Roshchupkin, V. P.; Enikolopyan, N. S. *Polym. Sci. U.S.S.R.* **1981**, ***23**(11)*, 2807.
(7) Burczyk, A. F.; O'Driscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255.
(8) Carlson, G. M.; Abbey, K. J.; U. S. Patent 4,526,945, **1985**.
(9) Janowicz, A. H.; U.S. Patent 4,694,054, **1987**.
(10) Hawthorne, D. G. WO Patent 87/03605, **1987**.
(11) Haddleton, D. M.; Muir, A. V.; Leeming, S. W. WO Patent 95/17435, **1995**.
(12) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3 (11)*, 365.
(13) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.
(14) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley & Sons, Inc.: New York, **1992**.
(15) Cacioli, P.; Hawthorne, D. G.; Laslett, R. L.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci.-Chem.* **1986**, *A23*, 839.
(16) Harrison, D. S., M.Sc. Thesis, Swinburn Institute of Technology, Victoria, Australia, **1988**.
(17) Meijs, G. F; Rizzardo, E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1990**, *C30(3&4)*, 305.
(18) Suddaby, K. G., Ph. D Thesis, University of Waterloo, Waterloo, Canada, **1994**.
(19) Chu, I. C.; Fryd, M.; Lynch, L. U.S. Patent 5,231,131, **1993**.
(20) Meijs, G. F, Rizzardo, E. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 547.
(21) Berge, C. T.; Darmon, M. J.; Antonelli, J. A. U.S. Patent 5,362,826, **1994**.
(22) Haddleton, D. M.; Padget, J. C.; Overbeek, G. C. WO Patent 95/04767, **1995**.
(23) Haddleton, D. M., Muir, A. V. WO Patent 95/04759, **1995**.
(24) Lin, J. C.; Abbey, K. J. U.S. Patent 4,6803354, **1987**.
(25) Lin, J. C.; Abbey, K. J. U.S. Patent 4,837,326, **1989**.
(26) Janowicz, A. H.; Melby, L. R. U.S. Patent 4,680,352, **1987**.
(27) Janowicz, A. H. European Patent Application 0 261 942, **1988**.
(28) Melby, L. R.; Janowicz, A. H., Ittel, S. D. European Patent 0 199 436 A1, **1986**.
(29) Janowicz, A. H. U.S. Patent 5,028,677, **1991**.
(30) Sanayei, R. A., Ph.D Thesis, University of Waterloo, Waterloo, Canada, **1989**.
(31) Rajatapiti, R.; Dimonie, V. L.; El-Asser M. S. *Polym. Mater. Sci. Eng.* **1994**, *71*, 57.
(32) Gridnev, A. A.; Goncharov, A. V. *Kinet. Katal.*, **1989**, *30*, 767.
(33) Gridnev, A. A. *Polym Sci.* U.S.S.R., **1989**, *31*, 2369.
(34) Greuel, M. P.; Harwood, H. J. *Polym. Prepr.* **1991**, *32*, 545.
(35) Marchaj, A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1992**, *31*, 4860.
(36) Gridnev, A. A. *Polym. J.* **1992**, *7*, 613.
(37) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.
(38) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.
(39) Dos Ramos, J. G.; Silebi, C. A. *Polym. Mater. Sci. Eng.* **1990**, *61*, 860.
(40) Dos Ramos, J. G.; Silebi, C. A. *Polym. Int.* **1993**, 30, 445.
(41) Suddaby, K. G., Maloney, D. R., Haddleton, D. M.; *Macromolecules*, submitted.
(42) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press Limited: London, **1995**.

MA960528H