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CATALYTIC CHAIN TRANSFER POLYMERISATION (CCTP) OF METHYL METHACRYLATE : EFFECT OF CATALYST STRUCTURE AND REACTION CONDITIONS ON CHAIN TRANSFER COEFFICIENT.

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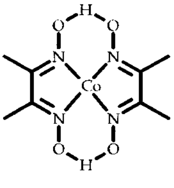
Abstract: Catalytic chain transfer polymerisation of methyl methacrylate has been investigated by a range of cobalt(II) complexes. The effect of catalyst structure, reaction temperature and solvent has been examined. At 60°C in the absence of solvent, the chain transfer coefficient, Cs, for MMA and cobaloximes modified by bridging BF_2 groups e.g. **3** is found to be 40,900, this is constant over a wide mass range. Cs is lowered when catalysts of larger cross sectional area are used supporting a diffusion controlled process. Co-ordinating solvents suppress Cs by competing for coordination of the Co(II) effectively reducing the concentration of active species. No conclusions can be drawn regarding the effect of temperature and thus the activation energy of the process. CCTP lowers the observed rate of polymerisation.

INTRODUCTION

The use of certain low spin cobalt(II) macrocycles as catalytic chain transfer agents (CCTA's) has emerged as an extremely effective method of reducing the molecular mass of poly(methacrylates) (Ref. 1-3). As the mechanism involves transfer of a hydrogen atom from the α-methyl of the terminal methacrylate group chain transfer activity is much lower for acrylates and styrene, etc. Chain transfer activity can be greater than 4 orders of magnitude larger than commonly used chain transfer agents such as mercaptans. This increased efficiency allows much lower quantities to be used thus avoiding problems associated with cost, colour, odour, etc. (Ref. 4) when using high levels of conventional chain transfer agent to achieve very low molar masses. Although quite a wide range of Co(II) macrocycles have been described the most effective are based upon



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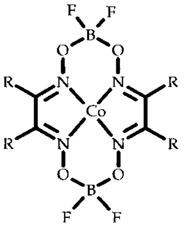

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cobaloximes, **1** (Ref. 5), and cobaloximes modified by bridging BF_2 groups, **2** (Ref. 6). The presence of the BF_2 group makes the catalyst more stable towards hydrolysis (Ref. 7) , thus easier to handle and applicable even in the presence of acidic monomers such as methacrylic acid under emulsion polymerisation conditions.

Although being described as early as 1979 and the subject of numerous patents the magnitude of the chain transfer coefficient for methyl methacrylate (MMA) and its dependence on reaction conditions i.e. solvent, temperature, etc. and catalyst structure remains unclear. The originally described catalysts were based on cobalt porphyrin e.g. the cobalt(II) complex of hematoporphyrin IX tetramethyl ether (Ref. 8). Application of the Mayo equation at conversions less than 10%, in the bulk and in benzene solution, produced values of Cs of (2.4 ± 0.1)E3. Cs was shown to be independent of temperature between 40-70°C and an excellent linear Mayo plot was obtained over the mass range Mn = 900-2400 thus showing chain transfer activity independent of catalyst concentration. The second generation cobaloxime CCTA, **1**, was described as having a Cs which varied dramatically from 2.0E4 to 2.28E3 on going from Mn = 500 to 186,000, in the bulk at 60°C (Ref. 6). This was ascribed to Cs being highly chain length dependent, in direct contradiction to Smirnov et. al. (Ref. 9) It is noted that the Cs in this study decreases when extremely small amounts of CCTA are employed. Analysis of results in the patent literature (Ref. 5) also using **1** with MMA proves interesting. Cs again increases when more CCTA is used but values reported are much lower ranging from 5E2 to 1.1E1 with Mn = 8,100 to 88,300. Although values here are somewhat erratic it appears that Cs generally increases with temperature (60,70 and 80°C). In all cases the highest reported Cs for MMA is 1.86E3. At very low mass we would expect Cs to decrease as monomer becomes a significant product, 100 being the lowest possible product mass, Cs must therefore decrease as this limiting low mass is approached.

The third generation catalysts containing BF_2 bridging groups **2** e.g. **3** where R = Me (CoBF) again show an increased chain transfer activity. The presence of the bridging groups result in greater hydrolytic and oxygen stability. Sanayei and O'Driscoll report Cs values of over 4E4 in bulk at 13% conversion (Ref. 6) . The Cs value is linear down to less than Mn = 2,000 where it decreases to 2.4E4 at Mn = 310. Chain transfer activity is described as decreasing with increasing temperature (60,70,80 and 90°C) resulting in a small, negative, activation energy, again in contrast to previous work. The Cs is described as being chain length dependent by analysis of the DRI trace from SEC. However, Gridnev has since demonstrated that the RI is mass dependent for these oligomers and thus this apparent chain length dependence may be due to this (Ref. 10). Chain transfer data for **2** and MMA can be obtained by analysis of the results from two separate patents, from DuPont (Ref.. 11) and CSIRO (Ref. 12). In both cases Cs is approx. 2E4. Interestingly the Cs stays *exactly* the same for each mass reported at Mn = 1470 to 60! Thus these authors do not see the expected lowering of Cs at very low mass due to MMA being as significant product. Cs is again shown to decrease on increasing temperature.

Thus, although chain transfer coefficients have been calculated for a range of catalysts under a range of conditions the results are ambiguous. It is noted that results taken from the patent literature are usually taken to high conversion which would give higher than expected Cs values by analysis with the Mayo equation. In very few cases have Cs values been calculated at significantly less than 10%. We have been interested to examine the effects of temperature, solvent, concentration, catalyst structure and monomer on Cs in order to further understand CCTP. This paper reports our initial results from this study.

EXPERIMENTAL

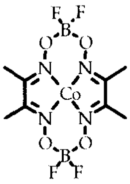
General methods and materials : All reactions were carried out using standard Schlenk apparatus and closed ampoules in a constant temperature water bath (±0.5°C). All reaction mixtures were deoxygenated by freeze-pump-thaw. Methyl methacrylate (MMA) was obtained from ICI and passed down a column containing basic alumina and 3Å molecular sieves under nitrogen prior to use, styrene was obtained from Aldrich passed down a basic alumina colum and deoxygenated by bubbling with nitrogen for 60 mins prior to use. Butanone was either used as received or vacuum distilled immediately prior to use, as described in the text. AIBN was obtained from BDH and recrystallised from methanol. All other reagents and solvents were purchased from Aldrich and used with no further purification. Bis(boron difluorodimethylglyoximate)cobaltate(II) **3** was prepared by the method of Espenson (Ref. 13) and recrystallised from methanol prior to use and used as the bis methanol adduct, as opposed to the bisaqua complex. Bis(boron difluorodiphenylglyoximate)cobaltate(II), **4** was prepared by replacing dimethylglyoxime with diphenylglyoxime in the synthesis of **3**. **4** was purified by washing with methanol, water and finally methanol prior to being dissolved in acetone and precipitated into methanol. **4** was also assumed to be the bis methanol adduct in calculating molar masses. Purification and characterisation of these Co(II) complexes is extremely difficult and care needs to be taken in ensuring catalyst batch deviations are avoided when determining and comparing Cs values.

Analysis : Size exclusion chromatography (SEC) was carried out using THF as an elutant at 1 ml min^{-1} with toluene (0.2 wt%) as an internal standard and flow marker in each sample. Two Polymer Laboratories Plgel 5μm Mixed-C columns (300 × 7.5 mm) and a PLgel 5μm guard column (50 × 7.5mm) were employed and calibrated with Polymer Laboratories PMMA standards from 200 - 1577000. Yields were calculated by drying a known weight of reaction mixture to constant weight in a vacuum oven.

Polymerisation : Stock solutions of (i) initiator in monomer (and solvent where appropriate) and (ii) catalyst in monomer were prepared. The appropriate amounts of each stock solution were added to an ampoule fitted with a Youngs vacuum tap. The monomer and, where used, solvent were added prior to a final deoxygenation via freeze-pump-thaw. The reaction mixtures were then immersed in a constant temperature water-bath for 15 minutes in the case of bulk reactions and 30 minutes where solvent was employed. For each set of reaction conditions 5 reactions were always carried out consisting of 4 different [monomer]:[catalyst] ratios (all using identical stock solutions) and a control containing no catalyst. In a typical polymerisation 2.5 mg of **3** was dissolved in 10 mL MMA, this was diluted by a factor of 10 to give a solution of 0.025mg mL^{-1} (5.57E-4 M). A stock solution of initiator was prepared by dissolving 150mg of AIBN in 24 mL MMA. Five reactions were prepared each containing a total of 5 mL, 4 mL of initiator solution and the remainder from a combination of catalyst solution and MMA, see table 1. After being deoxygenated and sealed all 5 reactions were heated simultaneously at 60°C for 15 mins prior to being cooled in ice. SEC was carried out on the reaction solution so as to avoid fractionation on precipitation.

RESULTS AND DISCUSSION

Catalytic chain transfer polymerisation of methyl methacrylate was carried out in the absence of solvent at 60°C under a range of [MMA]:[**3**] from 16,900,000 to 2,100,000:1 (mole ratio, in all cases the catalyst was assumed to be the bismethanol adduct so as to provide a molar mass), table 1. As expected we see a dramatic change in molar mass in each experiment. Even with a mole ratio of over 16,000,000 we see a reduction in Mn by approx. one quarter. The chain transfer coefficient, Cs, was calculated for each experiment and found to lie between 40,100 and 43,400 in all cases. The Mayo plot, figure 1, thus gives a linear plot with the Cs value of 40,900. The value obtained is in good agreement with that observed by O'Driscoll (Ref. 6) but twice that of other studies (Ref. 11). Cs is independent of concentration as expected. Earlier work has reported a concentration dependence when Mn is lowered to less than 1,000. Analysis of data at such low mass is open to large errors as there is a limiting low mass for product *viz.* 100 the mass of the monomer. This would certainly account for the lowering of Cs observed at relatively high catalyst levels by previous authors. We have observed no evidence for Cs being chain length dependent. We also do not observe a lowering of Cs at very low levels of catalyst as previously reported. However, in other experiments we have noted that when reagents are not rigorously purified and deoxygenated a lowering of Cs can be apparent, especially at very low catalyst levels. This is ascribed to degradation of catalyst by reaction with impurities. Thus at low conversion Cs for MMA with **3** is approx. 40,000 and is independent of catalyst concentration and thus mass of final product.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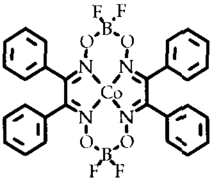
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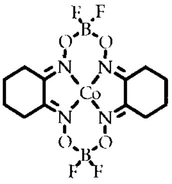
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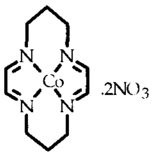
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Table 1: Summary of results for experiment 1, MMA/3/bulk/60°C

	Vol. catalyst soln./mL	Vol.MMA/ mL†	3/moles	MMA /moles	$\frac{[3]}{[MMA]}$	Mn/K	PDI	Cs¶	% conv.
A	0	5	0	4.69E-2	0	134.6	2.93	N/A	5.63
B	0.05	5	2.78E-9	4.69E-2	5.93E-8	32.07	2.13	40130	5.80
C	0.1	5	5.57E-9	4.69E-2	1.18E-7	17.78	2.22	41231	4.09
D	0.2	5	1.11E-8	4.69E-2	2.37E-7	9.09	2.14	43340	5.18
E	0.4	5	2.23E-8	4.69E-2	4.74E-7	5.00	2.12	40600	3.38

¶ Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [3]/[MMA], see figure 1, DP calculated from DP = Mn/100.12; † total volume, 4 mL from initiator solution and remainder as added monomer.

The effect of altering the ancillary ligands on the diimine are shown in table 2 and figure 1. Again with both catalysts, **4** and **5**, we see a constant Cs over a wide mass range. However, in both cases we see a lowering of Cs to 17,860 and 13,690, respectively. It is possible that this is a reflection of catalyst purity. However, the Cs value for this type of catalyst is believed to be close to the diffusion controlled limit. The cross sectional area of both **4** and **5** are obviously larger than **3**. This could well explain this lowering of Cs. Alternatively it is known that the strength of the Co- polymer bond is largely responsible for the catalytic activity. Both **4** and **5** may have stronger interactions with the polymer centred radicals in forming a Co(III)-alkyl. This is considered less likely as the presence of the four phenyl groups will increase the steric

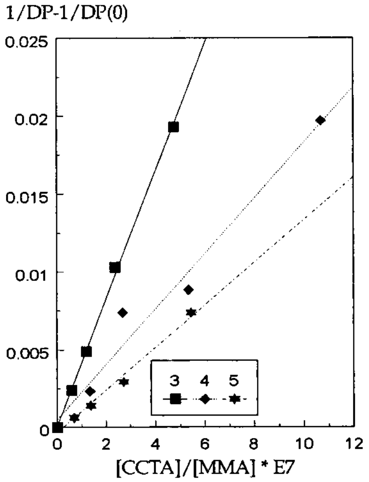

Figure 1 : Mayo plot for catalysts 3, 4 and 5 with MMA in the absence of solvent at 60°C

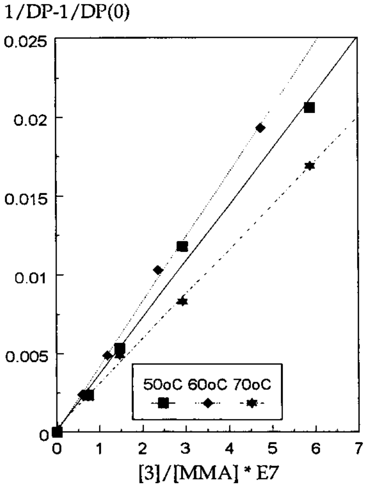

Figure 2 : Mayo plot for catalyst 3 with MMA in the absence of solvent for 50, 60 and 70°C

Table 2 : Summary of results for experiments 2[†] MMA/4/bulk/60°C/15 mins and experiment 3[‡] MMA/5/bulk/60°C/15 mins

	Catalyst **4**[†]					Catalyst **5**[‡]				
	$\frac{[4]}{[MMA]}$	Mn /K	PDI	Cs[¶]	% conv.	$\frac{[5]}{[MMA]}$	Mn/K	PDI	Cs[¶]	% conv.
A	0	197.8	2.32	N/A	4.59	0	145.6	2.10	N/A	6.21
B	1.34E-7	35.35	2.27	17400	4.36	6.80E-8	76.85	2.22	9040	6.02
C	2.67E-7	12.70	2.08	27582	3.83	1.36E-7	47.73	2.04	10360	5.67
D	5.35E-7	10.71	2.27	16533	3.95	2.72E-7	27.67	3.11	10770	5.37
E	1.07E-6	4.95	2.03	18453	3.62	5.44E-7	12.39	2.09	13580	4.96

[¶] Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [CCTA]/[MMA], see figure 1.

crowding above and below the plain of the ligand thus interacting with any axial ligand, such as polymer. These factors are currently under investigation by crystallographic and modelling studies in our laboratory. Thus at present we favour the reduced mobility of catalyst due to an increase in cross sectional area as the explanation for this phenomenon. However, results with styrene, see below, also support catalyst purity as the predominant factor.

When the experiments with **3** are carried out at 50, 60 and 70 °C, table 3, figure 2, we see no trend in Cs, again in contrast to earlier work (Ref. 6).This temperature represents a change in primary radical initiator half life from 300 to 5000 minutes. Thus we can draw no conclusions with regards to activation energy. Our data is over a relatively small temperature range but in each case over a wide mass range whereas previous data was over a larger temperature range but a less satisfactory mass range. Thus we are continuing to investigate this area.

Table 3 : Summary of results for experiments 4[†] MMA/**3**/bulk/50°C/60 mins and experiment 5[‡] MMA/**3**/bulk/70°C/5 mins

	Catalyst **3**, 50°C[†]					Catalyst **3**, 70°C[‡]				
	$\frac{[3]}{[MMA]}$	Mn /K	PDI	Cs[¶]	% conv.	$\frac{[3]}{[MMA]}$	Mn/K	PDI	Cs[¶]	% conv.
A	0	281.5	2.12	N/A	10.38	0	104.5	2.21	N/A	5.90
B	7.36E-8	37.43	1.87	31524	10.11	7.36E-8	28.8	1.96	34180	5.36
C	1.47E-7	17.58	1.98	36288	10.18	1.47E-7	17.1	1.96	33150	4.93
D	2.94E-7	8.23	1.91	40120	9.77	2.94E-7	10.8	1.81	28310	4.82
E	5.88E-7	4.78	1.81	34960	8.31	5.88E-7	5.62	1.81	28660	4.35

[¶] Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [3]/[MMA], see figure 2.

The effect of the polymerisation medium on Cs is very important. Experiments were carried out in methanol and both purified and unpurified butanone, tables 4 and 5, figure 3. Cs is lowered in all cases. The effect of butanone purification is quite dramatic with a change in Cs from 8020 to 26,500. Distillation of butanone removes trace acidic impurities. Although **3** is reported to be very acid stable our experiments with CCTP of methacrylic acid containing polymers under emulsion polymerisation show loss of catalytic activity ascribed to acid hydrolysis of **3**. The lowering of Cs in this case is thought to be due to poisoning of **3** by reaction of trace acid. The lowering from the bulk is most likely due to competition between MMA, butanone and polymer for reaction at the Co centre. In solution at the reaction temperature the Co will be co-ordinated to a solvent molecule. This would be MMA in the absence of other solvents. The lowered Cs suggests interaction of butanone with **3** is greater than for MMA with **3**. Thus the equilibrium shown in scheme 1 is expected to lie further to the left in the presence of a strongly co-ordinating solvent. This results in an increase in R_P/R_{CT} and a corresponding lowering of Cs. This effect is increased on moving to a more strongly co-ordinating solvent methanol. Crystals of catalyst grown in MMA solution at room temperature show methanol as the axial ligand even though there is a massive excess of MMA. Cs is lowered accordingly to 10,062. The use of methanol as solvent allows catalyst **6** to be investigated, **6** is insoluble in monomer. The Cs is 3 orders of magnitude lower than for **3-5** illustrating the sensitivity of activity to catalyst structure.

$$[\text{Co}]\text{-solvent} \leftrightarrows [\text{Co}] + \text{solvent}$$

Scheme 1

Catalytic chain transfer is most effective for monomers containing α-methyl groups such as methacrylates, the value of Cs being much lower for other monomers e.g. styrene, acrylates, etc. Nevertheless CCT agents are effective when compared to conventional chain transfer agents such as thiols. Table 6 reports the data for the CCTP of styrene in the bulk with catalysts **3** and **4**. In both cases Cs is relatively constant over a wide mass range and a significant reduction in Mn is observed. Cs values from Mayo plots, figure 4, give average values of 1392, **3**, and 702 , **4**. The absence of an α-methyl group means that the product must contain an internal unsaturated group, this is reflected in the reduction in Cs when compared to MMA.

Table 4 : Summary of results for experiment 6, MMA/3/methanol/60°C/30 mins, and experiment 7‡ , MMA/6/methanol/60°C/30 mins.

	Catalyst 3/methanol					Catalyst 6/methanol				
	[3]/[MMA]	Mn /K	PDI	Cs¶	% conv.	[6]/[MMA]	Mn/K	PDI	Cs¶	% conv.
A	0	50.42	2.41	N/A	5.44	0	106.6	2.48	N/A	7.17
B	2.97E-7	20.92	2.33	9435	3.31	2.84E-6	87.72	2.07	71.1	6.62
C	5.93E-7	11.36	2.24	11510	1.81	5.68E-6	33.61	2.85	359	3.61
D	8.90E-7	7.93	2.31	11950	2.33	1.13E-5	49.00	2.20	97.2	5.72
E	1.48E-6	6.10	2.43	9730	1.30	2.27E-5	37.94	2.45	74.8	5.58

¶ Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [CCTA]/[MMA], see figure 3.

However, the value of Cs is still 2-3 orders of magnitude greater than conventional chain transfer agents.

Table 5 : Summary of results for experiments 8, MMA/3/undistilled butanone/60°C/30 mins‡, and experiment 9, MMA/3/distilled butanone/60°C/30 mins†.

	Catalyst **3**‡					Catalyst **3**†				
	$\frac{[3]}{[MMA]}$	Mn /K	PDI	Cs¶	% conv.	$\frac{[6]}{[MMA]}$	Mn/K	PDI	Cs¶	% conv.
A	0	109.21	2.60	N/A	7.13	0	21.00	1.59	N/A	*
B	2.49E-7	73.83	2.36	1763	6.68	6.65E-7	8.17	1.68	11190	*
C	4.98E-7	37.34	2.37	3540	6.33	1.33E-6	3.44	1.84	18300	*
D	9.97E-7	13.59	2.43	6470	5.82	2.66E-6	1.37	2.13	25650	*
E	1.99E-6	6.20	2.25	7640	5.45					
F	1.99E-6	4.39	2.23	10980	5.01					

¶ Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [3]/[MMA], see figure 3; * conversion between 5 and 10 %.

The difference in activity between **3** and **4** is approximately the same for styrene as observed above for MMA. This indicates that the difference may be due to catalyst purity as with styrene the chain transfer is no longer diffusion controlled. This highlights a significant problem when investigating and utilising this chemistry. The purity of the catalyst is extremely important when comparing chain transfer coefficients from different laboratories and even experiments. Low spin Co(II) catalysts give poor quality NMR spectra, mass spectrometry is not quantitative and the compounds are relatively insoluble. Thus quantitative analysis is difficult especially as the exact nature of impurities is not fully understood.

Although not a focus of this study in all cases we observe a decrease in yield with an increase in catalyst concentration, in agreement with previous studies. Thus catalytic chain transfer decreases the rate of polymerisation. This is most apparent when the reaction is carried out in co-ordinating solvent, methanol, with **3** ,table 4, where a decrease from 5.44% to 1.30 % is observed.

CONCLUSIONS

Catalysts of general structure **2** are extremely effective catalytic chain transfer agents. Cs values are constant over a wide mass range. At very low levels of catalyst a reduction in Cs can be observed, especially in solvent, this is ascribed to poisoning by impurities of the very small levels of catalyst. At high catalyst concentration Cs is also reduced which is a result of the lowest possible product mass being 100, in the case of MMA. This gives S shaped Mayo plots which

Table 6 : Summary of results for experiments 10, styrene/3/bulk/60°C/30 mins‡, and experiment 11, styrene/4/bulk/60°C/30 mins†.

	Catalyst 3‡					Catalyst 4†				
	$\frac{[3]}{[STY]}$	Mn /K	PDI	Cs¶	% conv.	$\frac{[4]}{[STY]}$	Mn/K	PDI	Cs¶	% conv.
A	0	69.86	1.88	N/A	1.60	0	68.11	2.11	N/A	1.59
B	5.10E-6	10.12	2.42	1724	1.36	1.74E-6	37.52	1.86	714	1.49
C	1.02E-5	6.60	2.12	1398	1.34	3.49E-6	28.61	1.81	605	1.35
D	1.53E-5	4.38	2.12	1456	1.20	5.23E-6	20.62	1.79	672	1.29
E	2.04E-5	3.44	2.13	1409	1.17	6.98E-6	15.98	2.02	714	1.20

¶ Calculated from Mayo equation applied to a single point, true Cs from plot of 1/DP against [CCTA]/[STY], see figure 4.

Table 7 : Chain transfer constants as calculated from application of the Mayo plot for experiments 1 - 11.

Experiment	Catalyst	Temp/°C	Solvent	Monomer	Cs*
1	**3**	60	none	MMA	40900
2	**4**	60	none	MMA	17860
3	**5**	60	none	MMA	13690
4	**3**	50	none	MMA	35582
5	**3**	70	none	MMA	28120
6	**3**	60	methanol	MMA	10062
7	**6**	60	methanol	MMA	77
8	**3**	60	butanone(undistilled)	MMA	8020
9	**3**	60	butanone (distilled)	MMA	26500
10	**3**	60	none	styrene	1392
11	**4**	60	none	styrene	702

can be avoided by working at low conversion in the correct mass range. Cs is lowered in co-ordinating solvent due to competing reactions. Increasing the cross sectional area of the CCTA reduces Cs and this is evidence that the process is diffusion controlled. Although contributions from impurities cannot yet be discounted. Thus this class of chain transfer agents may represent the limiting efficiency possible. Although Cs is much lower for styrene it is still considerably higher than conventional chain transfer agents.

ACKNOWLEDGEMENTS

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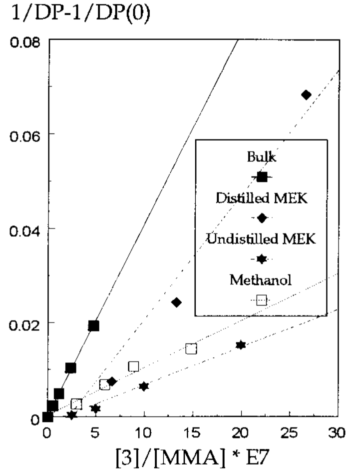

Figure 3 ; Mayo plot for **3** in the absence of solvent, methanol and distilled and undistilled butanone

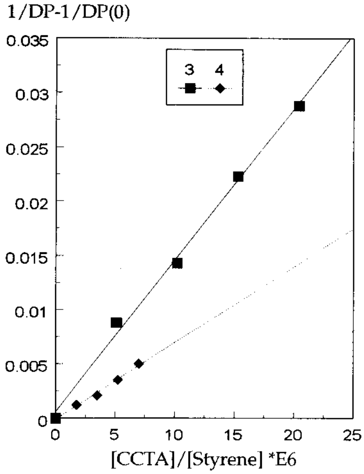

Figure 4 : Mayo plot for catalysts **3** and **4** with styrene in the absence of solvent

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