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Tying Up Loose Ends: Some Mechanistic Aspects of Catalytic Chain Transfer

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SUMMARY: Polymerisation of methyl methacrylate in the presence of two catalytic chain transfer agents has been investigated. Several factors were examined to see how they would affect the chain transfer process. Oxygen and initiator impurities added to the system were found to be detrimental. The transfer process was highly intolerant of initiator impurities, but was able to endure a large excess of oxygen. The temperature dependencies of the chain transfer process were determined for cobaloxime boron fluoride (COBF) and cobalt(*meso*-Ph_4-porphyrin) (CoP). The results showed that a study of MW, or k_{tr} would be a better gauge of the catalyst activity. Activation energies were determined at two concentrations of initiator and it was discovered that the transfer process has a dependence on the initiator concentration. A mechanism for this dependency is proposed that involves a reduction in the active catalyst concentration. As a result, the measured values for C_{tr}, and k_{tr}, must be apparent values. An additional consequence of the initiator dependence is that the MW of the polymer products will be directly dependent on the concentration of the initiator.

Introduction

The catalytic chain transfer (CCT) polymerisation of methacrylates by cobalt(II) square planar complexes has been investigated for almost 20 years$^{1\text{-}7)}$. CCT is of increasing interest because it is an environment-friendly method of producing macromonomers, and this is important to industry. The conventional methods of producing desired, low molecular weight oligomers involve the use of large quantities of initiator (typically a peroxide) and transfer agents (typically sulfur-containing compounds). In addition to the undesirable environmental effects of these chemicals, the sulfur compounds add odor and color. Although CCT is a well known method for producing macromonomers, the mechanism of this process and the factors that affect it are still poorly understood. Scheme 1 shows the accepted mechanism for CCT$^{4,8)}$. The initial step must be the first addition of a cobalt(II) species to a growing radical chain to begin chain transfer. The resulting, undetected, cobalt-hydride species reinitiates

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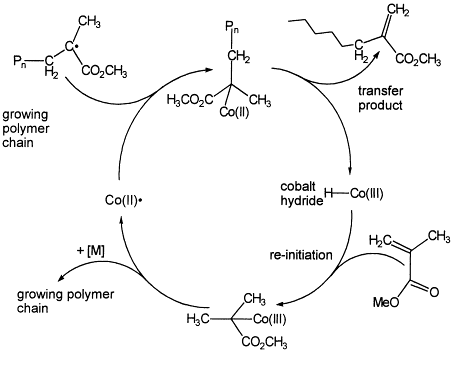
propagation by transferring a hydrogen to a monomer unit. The net process results in the catalytic cycle regenerating the Co(II) complex.



Scheme 1

$$R_n \bullet + Co(II) \rightarrow P_n + Co(III) - H \quad (1)$$

$$Co(III) - H + M \rightarrow R_1 \bullet + Co(II) \quad (2)$$

$$\frac{1}{DP_n} = (1+\lambda)\frac{k_t[R\bullet]}{k_p[M]} + C_M + \frac{k_{tr}[Co(II)][R\bullet]}{k_p[M][R\bullet]} \quad (3)$$

Equations 1 and 2 describe the essential steps in the cycle. Assuming that the first step is the rate determining step leads to the Mayo equation (eq. 3)[9, 10]. This is the generally accepted equation that relates the degree of polymerisation (DP) to the types of termination that are present. The first term involves termination by combination, where λ is the fraction of termination by disproportionation. C_M involves direct transfer to monomer. CCT is transfer-dominated and thus the molecular weight should be based on the last term. Recent papers have shown that the Mayo method is comparable to the chain length distribution (CLD) method if DP_n is obtained by using $M_w/2$ instead of M_n[9]. The Mayo method will be used here since it is a much simpler method. The transfer constant, C_{tr}, is the usual constant employed to determine the effectiveness of a transfer agent and is simply the ratio of k_{tr} to k_p. A plot of the Mayo equation, as $1/DP_n$ vs. [CTA]/[M] (where CTA is the chain transfer agent), should yield a straight line whose slope is C_{tr}. Since the radical concentration can be cancelled out of the last term in the Mayo equation, the MW should be independent of the number of radicals.

In this paper we will examine the effects of various impurities and reaction conditions on the CCT process. In conjunction with these findings we will examine the dependence of CCT on initiator concentration and discuss why this system appears to be sensitive to the amount of initiator. Two catalyst systems will be examined: COBF and the cobalt porphyrin complex, Co(*meso*-Ph_4-porphyrin), CoP, in bulk MMA with AIBN initiator.

Experimental

Materials: MMA was distilled and then passed through a column of alumina, deoxygenated with argon, and placed over molecular sieves. Azobisisobutyronitrile (AIBN) was recrystallised twice from EtOH or MeOH and then stored in the glovebox. COBF (bis(aqua)bis((difluoroboryl)dimethylglyoximate) cobalt(II)) was prepared according to a procedure of Bakac and Espenson 11). It was analysed using UV-Vis spectroscopy and elemental analysis (experimental C: 23.0 %, H: 3.91 %, N: 13.5 %; calculated C: 22.8 %, H: 3.83 %, N: 13.3 %). One single batch was used for all experiments.

Polymerisations: For each experiment 6-8 samples were prepared. A wide range of [Co]/[M] ratios were used, to ensure that an adequate, straight line Mayo plot could be obtained. A typical plot is shown in Fig. 1. All solutions and samples were prepared inside a glovebox (O_2 < 1 ppm) to ensure that oxygen and other impurities were kept to a minimum. A thermostatted waterbath was used to regulate the temperature to +/- 0.1 °C. Reactions were terminated by addition of hydroquinone and cooling. Monomer was evaporated and the polymer dried under vacuum at 40°C. Conversion was determined gravimetrically.

Analyses: Size exclusion chromatography (SEC) was carried out using THF as an eluent at a flow rate of 1 mL•min^{-1}. Two Polymer Laboratories PLgel 5 μm Mixed-C columns (300 x 7.5 mm) and a PLgel 5 μm guard column (50 x 7.5 mm), calibrated with Polymer Laboratories polystyrene standards, were used. The polystyrene calibration curves were converted by universal calibration using Mark–Houwink parameters: K_{MMA}= 0.994x10^{-4}dl/g, a_{MMA}= 0.719.

Results and Discussion

The initial investigations were carried out to determine the effect of impurities on the system. Literature mentions that the AIBN initiator in these systems needs to be recrystallised twice before use, but the source of any impurities is not mentioned8, 12, 13). To examine what effects impurities might have, it was first necessary to establish a repeatable, standard procedure for the cobalt-mediated MMA polymerisation. The conditions of this procedure involve the careful handling of reagents as mentioned above. Fig. 1 shows the Mayo plot for a typical experiment. Any changes that affect the catalytic cycle should affect the slope and be readily observable.

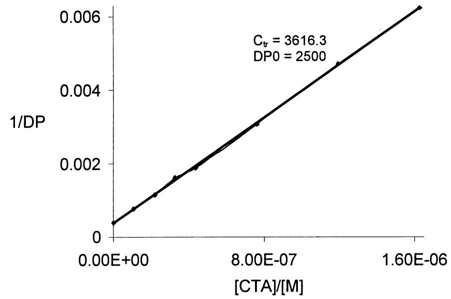


Fig. 1: Mayo plot for CoP at 80°C

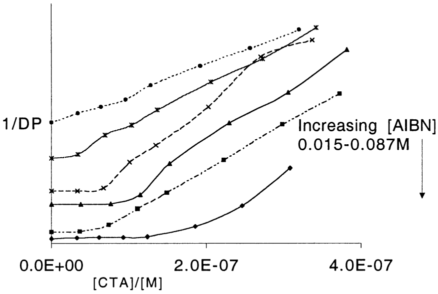


Fig. 2: Mayo plots for COBF/MMA with varying [AIBN]. Data is offset for clarity

Fig. 2 shows plots of the effects of using AIBN which has not been purified. As more initiator is added to the system the amount of inhibition increases. This indicates that there is an impurity irreversibly binding with the COBF catalyst. At a certain point the slope of 1/DP vs. [CTA]/[M] seems to return to the same value as seen for low [AIBN]. At this point the impurity has been consumed, and the product is not involved in further reaction. Attempts were made to determine the source of the impurity in AIBN. Two experimental factors needed to be examined to obtain reliable results. The first was consistency in the use of the cobalt catalyst. Several papers have mentioned that repeatability in these investigations depends on the purity of the cobalt catalyst and therefore all reactions should be done with only one batch of the catalyst[12, 13)]. Since very small amounts of catalyst are required for this process, it is usual to make up a stock solution (~10^{-4}M). This stock solution is further diluted to obtain a working solution (~10^{-5}-10^{-6}M) from which aliquots will be used in the actual experiments (10^{-7}-10^{-8}M) . The 10^{-4}M stock solution of COBF was found to be stable inside the glovebox for at least several months. Thus, most of the work presented here was carried out with a single 10^{-4}M stock solution of catalyst. The second reliability factor was the stability of the AIBN itself. Since it is a thermally unstable compound and the presence of an impurity was demonstrated above, we wished to see if this impurity could be reintroduced to the recrystallised AIBN. Heating samples of AIBN or prolonged storage, in both the glovebox and under normal atmospheric conditions, did not result in the reappearance of the impurity. Therefore it appears that this impurity is introduced during manufacture, and that the AIBN can be reliably used for long periods after recrystallisation. From Fig. 2, an estimate was made of the concentration of the impurity in AIBN. A value of about 0.002 mol% was found, based on the assumption that the impurity reacts irreversibly to form a 1:1 compound with the cobalt species.

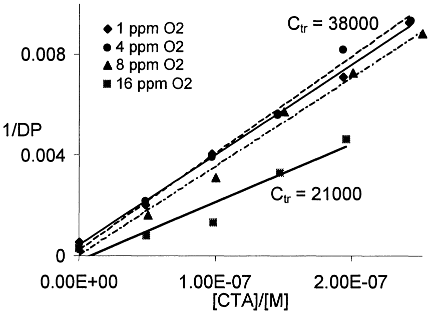


Fig. 3: Mayo plots for the sequential addition of oxygen to COBF/MMA/AIBN at 60°C.

The next factor to be examined was the effect of oxygen on the transfer process. Reliable results were only obtained when the MMA had been thoroughly deoxygenated before use. Deoxygenation is a common feature of other experimental procedures[12, 13)]. An oxygenated solution of MMA was prepared by bubbling it with air for about an hour and then using it to make up the stock initiator solution. The last step in sample preparation was to add aliquots of the oxygenated initiator solution to the catalyst solutions. Thus, exposure of the cobalt to oxygen was kept to a minimum before initiation. The results are shown in Fig. 3. Surprisingly enough, the effects of the oxygen were much less noticeable than expected. Whereas long term exposure of cobalt to oxygen was detrimental, short term exposure did not present a large problem. It was not until large excesses of oxygen were present (~20 ppm; 1 ppm $O_2 \approx 10^{-5}$ M) that there was a significant effect on the transfer constant. It appeared that oxygen did not have a significant effect on the transfer process, other than to react slowly with the Co(II) species.

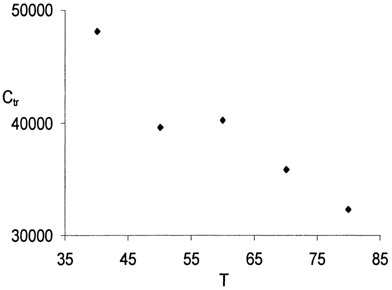


Fig. 4a: C_{tr} vs. T for COBF/MMA/AIBN

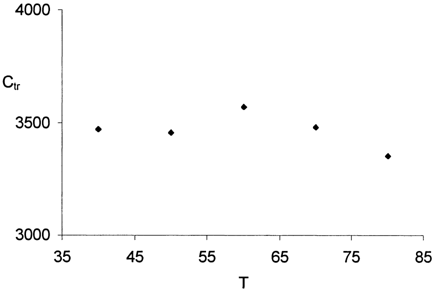


Fig. 4b: Ctr vs. T for CoP/MMA/AIBN

The issue of temperature dependence in CCT has not been resolved in the literature. In fact, there have been conflicting reports about the effects of temperature on C_{tr} for COBF in MMA[8, 12-14)]. Heuts et al.[14)] reported that there is no noticeable affect on C_{tr} when the temperature is varied from 40-70°C and therefore conclude that the activation parameters for this process must be similar to the values for propagation. Other reports claim that there is an inverse dependence of C_{tr} on temperature[8, 13)]. This leads to a negative activation energy for the transfer cycle. The negative activation energy can happen because C_{tr} is the ratio of two different processes, chain transfer and propagation, and it simply indicates that E_a for transfer is smaller, and therefore less temperature dependent, than E_a for propagation[15)]. We found that C_{tr} for COBF shows an inverse dependence on temperature, while for CoP there is no temperature dependence (Fig. 4).

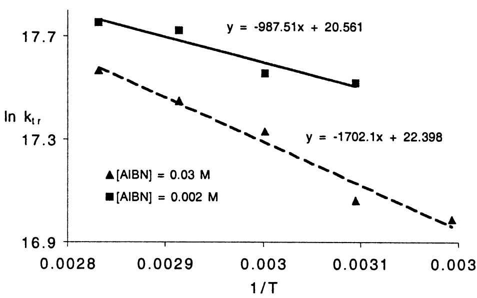


Fig. 5a: Arrhenius Plot for COBF/MMA/ AIBN at two initiator concentrations

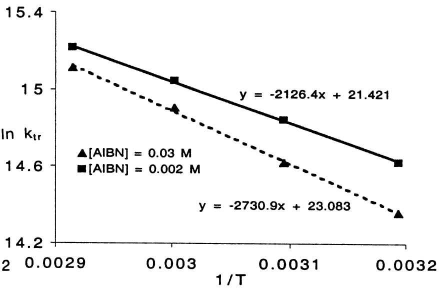


Fig. 5b: Arrhenius Plot for CoP/MMA/ AIBN at two initiator concentrations

Alternatively, Arrhenius plots for k_{tr} provide more detail in the form of activation parameters (Fig. 5 and Table 1) at two initiator concentrations. C_{tr} is temperature independent for CoP, thus E_a for transfer is almost the same as for propagation.

Table 1. Activation parameters for transfer.

catalyst[a]	E_a (kJ/mol)	A ($s^{-1}M^{-1}$)
COBF $2x10^{-3}$M	8.2	9×10^{8}
COBF $3x10^{-2}$M	14.2	5×10^{10}
CoP $2x10^{-3}$M	17.7	2×10^{9}
CoP $3x10^{-2}$M	22.7	1×10^{10}
propagation[b]	22.34	$2.65x10^{6}$

a. Concentration of AIBN
b. From ref. [15)]

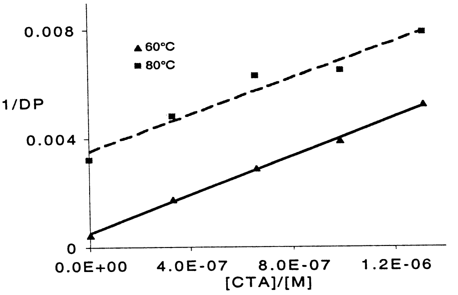


Fig. 6: Mayo plot for CoP/MMA/AIBN at 60° and 80°C.

The examination of C_{tr} and k_{tr} still ignores some basic information. Ultimately, it is the MW of macromonomers produced that is the most significant quantity in determining the effectiveness of the catalytic system. Fig. 6 shows the Mayo plots at 60°C and 80°C using CoP with MMA. Although it is apparent that C_{tr} (the slope) is almost constant at the two temperatures, the DP is much lower at the higher temperature. A similar analysis for COBF shows that the MW of the products is almost invariant with temperature (in the high [Co] regime) although the value of C_{tr} decreases significantly with temperature (Fig. 4a). Thus, for COBF, an examination of only C_{tr} will indicate that high temperature is detrimental, while in fact the MW is virtually temperature independent. These observations are a clear indication that the termination term of the Mayo equation is also important in determining DP. At these relatively high levels of initiator and at the higher temperature examined, molecular weights in the absence of catalyst are often well below 10^5. At lower initiator concentrations, the MW obtained at 0 catalyst loading will be significantly higher, and the effect of termination will be less important than the dependence of C_{tr} on temperature.

We also examined whether the initiator concentration can affect CCT. Fig. 5 shows the surprising result of obtaining Arrhenius plots at two initiator concentrations for COBF and CoP. It is evident that there is a significant and constant effect due to changing the initiator concentration. The chain transfer process becomes more efficient at lower radical flux suggesting that the extra radicals are involved in a process which is slowing down the overall cycle. Based on information we have on other reactions16) we believe that the retardation process is caused by an equilibrium in the first step of transfer, the initial combination of radical and cobalt. This equilibrium causes a reduction in the active catalyst concentration. We see this as a reduction in C_{tr} at higher initiator concentrations. As a result, reported transfer values will not be intrinsic values but will instead be lower, observed values. The explanation of the interaction between the cobalt catalyst and the radicals is still being examined and will be discussed further in future work. It is important to note that the effect of the Co-radical equilibrium is different from the irreversible binding caused by impurities in the AIBN, and has the opposite effect of bimolecular termination.

Conclusion

The results of our studies have clearly shown several trends and new considerations for the analysis of catalytic chain transfer. First of all, it was shown how the catalysis of COBF is inhibited by impurities. An impurity in the initiator appears to be introduced during the manufacturing process and irreversibly binds the catalyst. The system is more robust towards oxygen. If the cobalt is only minimally exposed to oxygen before initiation then the system can withstand even relatively high concentrations of oxygen.

The effects of changing the temperature and radical concentration were also examined. It was shown that the effects of temperature on the molecular weight cannot be judged by only examining C_{tr}. At higher radical flux (higher initiator concentration and/or higher temperature) the bimolecular termination contributes considerably to the overall reduction of the molecular weight. Most surprisingly, and previously overlooked, the radical concentration affects the catalytic cycle such that a decrease in radical concentration increases the effectiveness of the cobalt catalyst. The reason for this is not clear as yet, but it appears that there is some interaction between the radical and the cobalt, causing a decrease in the active catalyst concentration upon increasing the radical concentration. This important effect is complicating the analysis of C_{tr} as a function of temperature and will be the topic of a forthcoming paper.

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