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Chain transfer in pulsed laser polymerization of methylmethacrylate in the presence of different cobalt (II) [Co(dmg-2H)$_2$ (BF$_2$)$_2$] and [Co(afdo-2H)$_2$ (BF$_2$)$_2$] complexes

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Abstract

Methylmethacrylate (MMA) was polymerized at 25 °C with excimer laser (λ = 308 nm) in the presence of different Co(II) chain transfer agents, bis(boron difluorodimethylglyoximate) cobaltate(II) [Co(dmg-2H)$_2$ (BF$_2$)$_2$] (henceforth called catalyst (1)) and bis(boron difluorodialphafurilglyoximate) cobaltate(II) [Co(afdo-2H)$_2$ (BF$_2$)$_2$] (henceforth called catalyst (2)) used separately, with 2,2′-Azobis-(2-methylpropionitrile) [AIBN] as an initiator. The polymer (PMMA) formed in this study was characterized using GPC, ^{1}H NMR, ^{13}C NMR, and DEPT 135. The value of chain transfer constant (C_s) was higher for catalyst (1) than catalyst (2) by a factor of 5. The higher character of "living free radical polymerization", as evident from the low values of polydispersity index (PDI), was observed mainly for catalyst (2). Both steric and electronic factors supported by IR and UV–vis spectra for the two catalysts indicate that catalyst (2) is a weaker nucleophile as compared to catalyst (1) forming a weaker Co–C bond between this catalyst and growing polymer chain indicating more living polymerization for the catalyst (2).

Keywords: Pulsed laser polymerization; Cobalt (II) catalysts; Chain transfer constant; Methylmethacrylate

1. Introduction

Ever since Enikolopyan and co-workers [1] reported the catalytic chain transfer to monomer in radical polymerization, it has been established that some cobalt chelates complexes of cobalt (II) [2] catalyze transfer of hydrogen from a free radical to an olefin. Enikolopyan and co-workers [1] proposed the mechanism for catalytic chain transfer (CCT) with a modified catalytic cycle shown in Scheme 1. In CCT, initiation, propagation, and termination occur as in a normal free radical polymerization, with the addition of the transfer reaction. It may be remarked that the objective here is to restrict the size of the polymer and the rate of polymerization in terms of the desirable chain length and molecular weight beyond which its material properties such as mechanical strength do not change significantly. The chain transfer agent facilitates this process by introducing additional pathways by intercepting the growing polymer free radical chains. In that sense it may be reasonable to designate the chain transfer agent (CTA) as a catalyst, even though the role of the CTA is to restrict rather than enhance the polymerization process, contrary to the common perception of a catalyst as an enhancer of the process.

In the case of [LCo(II)] complexes, e.g., catalyst (1) in Fig. 1, an unpaired electron in the dz^2 orbital of Co-atom attacks Pz orbital of sp^2 hybridized C-atom of growing polymer chain Rn to produce [L(Co(III)Rn]. However, this step is believed to be reversible as shown in Scheme 2. From [L(Co(III)Rn], β-elimination takes place yielding dead polymer chain (P_n) with a terminal double bond and [LCo(III)H]. For the sake of simplicity, the methyl group on the dimethyl glyoxime (H$_2$dmg) ligands has been omitted for the remaining steps in the cycle. Markonikov regioselectivity for the addition of MMA via insertion to [LCo(III)H] results in a more weakly bonded tertiary alkyl complex [LCo(III)-C(CH$_3$)$_2$CO$_2$CH$_3$], which is an important consequence of the hydrogen atom transfer mechanism [3]. This subsequently dissociates to produce a monomeric radical (which then propagates to form growing polymer or oligomer

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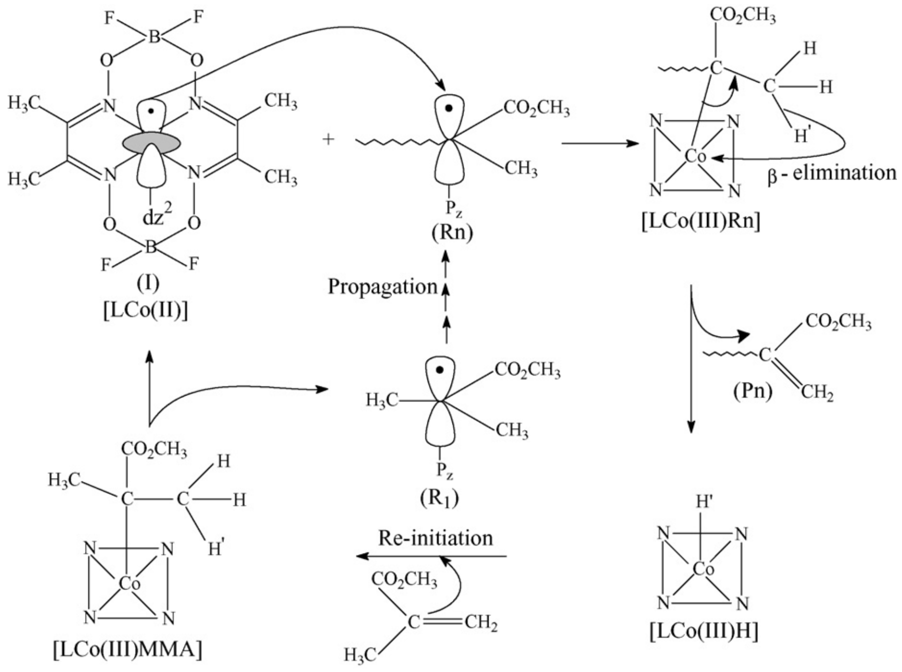


Scheme 1. Catalytic chain transfer mechanism for Co(II) catalyst for polymerization of methylmethacrylate.

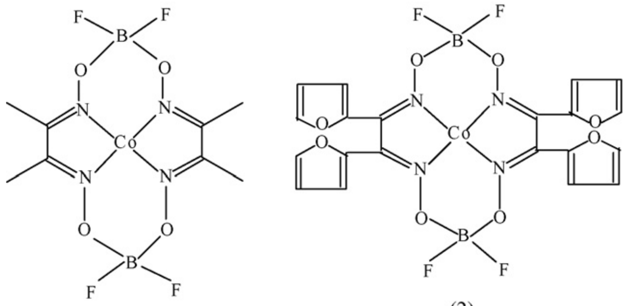
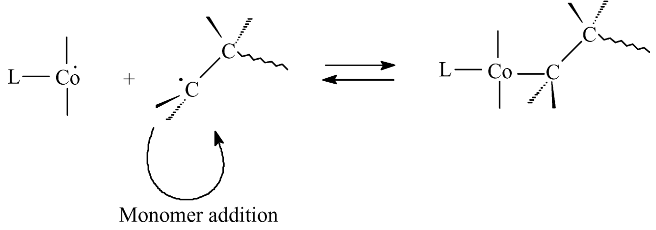

(1) (2)

Fig. 1. Co(II) catalysts used as chain transfer agents for pulsed laser polymerization of MMA.

chain) and the starting LCo(II) catalyst. Re-initiation in catalytic chain transfer takes place with the rate constants considerably faster than that in mercaptans (usually used as a catalyst).

Formation of the Co–C bond in some cases such as free-radical polymeriztion of acrylates in the presence of Co(II) complexes is reversible as shown in Scheme 2, thus producing "living radical polymerization" (LRP) [4–6]. Metalloradical mediated LRP requires that the only reaction of the metalloradical is to bind reversibly with the growing polymer radical to produce a constant equilibrium concentration of propagating polymer radicals [7]. Chain transfer catalysis occurs when the metalloradical abstracts a β-H from the growing polymer radical to form a metal hydride that reinitiates polymerization between [LCo(III)H] and monomer (MMA) [8–11]. The chain transfer constant for a catalyst depends not only on the steric hindrance but also on the electronic factors (such as nature of the chelating ligands and other ligands attached at the axial position) of the catalyst. Wayland et al. [6] reported that for free radical polymerization of methyl methacrylate by cobalt (II) porphyrin complexes, chain transfer catalysis is best achieved when there are minimal steric demands. This allows β-H abstraction from oligomer radical by $M^{\bullet}$, as noted in the radical polymerization of methyl methacrylate in the presence of tetraanisylporphyrinato cobalt(II). When β-H abstraction from the oligomer is precluded by sterics, a metalloradical mediated living radical polymerization can occur.



Scheme 2. Living radical polymerization of MMA in the presence of chain transfer agent.

In this paper, we present a comparative study of two different catalysts for chain transfer in pulsed laser polymerization of MMA at 25 °C using an excimer laser (XeCl at 308 nm). We synthesized and characterized bis(boron difluorodimethylglyoximate) cobaltate(II) [$Co(dmg\text{-}2H)_2(BF_2)_2$] and bis(boron difluorodialphafurilglyoximate) cobaltate(II) [$Co(afdo\text{-}2H)_2(BF_2)_2$], called catalysts (1) and (2), respectively (Fig. 1), to determine their respective roles as chain transfer catalysts. So far, there are only a few isolated reports on experimental data for catalytic chain transfer in photo-polymerization. More specifically, Forster et al. [12] have recently reported photo-polymerization of 2-phenoxymethyl methacrylate with COPhBF as chain transfer agent at 60 °C, using a Nd:YAG laser with a third harmonic generator to produce 355 nm UV radiation. To the best of our knowledge, pulsed laser polymerization of MMA using

[Co(afdo-2H)$_2$ (BF$_2$)$_2$] catalyst as chain transfer agent has not been reported so far.

2. Experimental

2.1. Materials

The MMA (>99%) from Fluka was mixed with 10% NaOH to remove inhibitor. It was then washed with distilled water. Residual amount of water was removed by adding anhydrous sodium sulfate. The monomer was distilled [13] under dry nitrogen at 58–60 Torr pressure and 33–35 °C. AIBN was recrystallized with CH_2Cl_2. Methanol from BDH was used as received.

2.2. Catalyst preparation

The catalyst (1) was prepared according to the procedure reported earlier by Bakac et al. [14] with slight changes. Initially 0.9887 g of dimethyl glyoxime [H$_2$dmg] (8.514×10^{-3} mol) was dissolved in 100 ml of ether. Then 0.9986 g (4.010×10^{-3} mol) of cobaltous acetate was added. After 45 min of stirring, 10.0 ml of etherated BF_3 was added and the solution was refluxed for 24 h. To the resulting suspension, ice-cold water was added and the solution was filtered. The precipitates were washed with water, methanol and ether and dried under vacuum at room temperature. Catalyst (2) [Co(afdo-2H)$_2$(BF$_2$)$_2$] was synthesized in a similar way.

For characterization, the solid state IR spectra of the complexes were recorded in the range 3700–450 cm^{-1}on Perkin-Elmer 16 FPC FT-IR using KBr pellet with eight scans and a resolution of 4. The UV–vis spectra of the ligands and complexes in DMSO were recorded in the range 500–200 nm on Perkin-Elmer Lambda 5 spectrophotometer. The following instrumental conditions were used: slit = 2 nm, scan speed = 60 nm/min, response = 0.2 s, peak threshold = 0.02 A.

2.3. Pulsed laser polymerization

A stock solution of [Co(dmg-2H)$_2$(BF$_2$)$_2$] catalyst (1) was prepared by dissolving 1.0 mg of the catalyst in 10.0 ml of freshly distilled MMA already containing 10.0 mg of AIBN. Then, 5.0 ml of stock solution was diluted to 16.0 ml so that the final solution concentration was 7.40×10^{-5} M. A second initiator stock solution was prepared by dissolving 50.0 mg AIBN (6.1×10^{-3} M) in 50.0 ml of MMA. Five reaction mixtures were prepared, each containing 6.0 ml of initiator solution except the last one and 0.0, 0.2, 0.6, 0.8, and 1.0 and 2.0 ml of the catalyst (1) stock solution. Similarly, a stock solution of [Co(afdo-2H)$_2$(BF$_2$)$_2$] catalyst (2) was prepared by dissolving 1.0 mg of the catalyst in 5.0 ml of freshly distilled MMA already containing 5.0 mg of AIBN. A second initiator stock solution was prepared by dissolving 35.0 mg AIBN in 35.0 ml of MMA. Five reaction mixtures were prepared, each containing 6.0 ml of initiator solution and 0.1, 0.2, 0.3, 0.4, and 0.5 ml from catalyst (2) stock solution. The dissolved O_2 was removed by freeze-pump-thaw operation and finally the test tubes were sealed. Then the solution of each test tube was transferred to 4.0 ml capacity quartz cell under dry nitrogen gas.

The experimental details have been presented in an earlier report [15] and are similar to Olaj et al. [16]. We used, a XeCl excimer laser (Lambda Physik Model EMG 203) giving UV light at 308 nm wavelength. This pulsed laser was operated at 10 Hz. Each laser pulse was of 20 ns duration and carried 150 mJ of energy. The laser beam was directed towards the cell with the help of a 100% reflecting mirror. The laser beam spot size at the position of the cell was 10 mm × 30 mm and covered most of the volume of the sample cell. No focusing or beam expansion was needed in this case. The laser energy per pulse incident on the cell was measured with the help of a beam splitter that directed about 10% of the energy to a photodiode. The signal from the photodiode was read by a two-channel oscilloscope (Tektronics 2465). On the other hand, the residual laser energy per pulse transmitted by the cell was measured with a Molectron J-50 probe. Again, the signal from the probe was read by the same oscilloscope. We measured the reference energy without the cell and then the energy transmitted by the empty cell. Even without the sample, this indicated about 16% loss due to reflections at the four surfaces, two for each wall (front and the back) of the cell. Subsequently, we measured the energy transmitted by the cell containing the samples. This gave some useful information about the laser light absorbed by the sample.

Each sample was exposed to the laser radiation for 45 min. In this time, 27,000 pulses (i.e., 45 min × 60 s/min × 10 pulses/s) interacted with the sample. Since each pulse was of 20 ns duration, the net exposure time (assumed continuous) was 0.54 ms (i.e., 27,000 pulses $\times (20 \times 10^{-9})$ s/pulse $= 0.54 \times 10^{-3}$ s). The resulting polymer was added in 60 ml of methanol under constant stirring. Initially, all the methanol and residual MMA was evaporated. The PMMA was subsequently dried in a vacuum at 25 °C.

3. Results and discussion

3.1. Characterization of chain transfer agents

Both the chain transfer catalysts were characterized by melting point, UV–vis and IR spectroscopy, and elemental analyzer. Calculated values (%) for [Co(dmg-2H)$_2$(BF$_2$)$_2$·2H$_2$O] were: C = 22.8; H = 3.8; and N = 13.3; while the experimentally measured values were: C = 23.2; H = 3.7; and N = 13.8. Similarly, calculated values (%) for [Co(afdo-2H)$_2$(BF$_2$)$_2$·2H$_2$O] (%) were: C = 38.2; H = 2.5; N = 8.9; while the experimentally measured values were: C = 37.3; H = 2.4; and N = 8.5.

3.1.1. Electronic spectroscopy

The cobalt(II) complexes of both α-furilglyoximes (H$_2$afdo) and dimethylglyoximes (H$_2$dmg) ligands were analysed by IR and UV–vis spectroscopy. The IR signals recorded for the catalysts were in accord with literature reported values [17,18]. The C=N peak at 1364 cm^{-1} for free H$_2$dmg ligand is shifted to 1386 cm^{-1}. Moreover, there is a significant $p_{\pi*} \leftarrow d_{\pi}$ back bonding resulting in higher C=N characters with concomitant increase in C=N vibrational frequency. In the case of

$[Co(afdo\text{-}2H)_2(BF_2)_2]$ catalyst, the two sharp peaks due to water molecules appeared at 3570 and 3628 cm^{-1}, which is an indication that σ-donation of electron from water molecule (axial ligand) is higher in this complex as compared to catalyst (1) resulting in more back bonding in case of catalyst (2) as compared to catalyst (1). Another indication of comparatively strong $p_{\pi^*} \leftarrow d_{\pi}$ back bonding in catalyst (2) is the appearance of Co–N stretching vibrations at higher wave numbers (504 and 542 cm^{-1}) as compared to catalyst (1) in which Co–N stretching vibrations appear at lower wave numbers (464 and 502 cm^{-1}) [19].

From our measurements on a UV spectrophotometer, we note that ligand-to-metal charge transfer transitions (LMCT) in both the complexes take place almost at the same wavelength, i.e. 270 nm. According to the selection rules that are used to differentiate between charge transfer transitions and ligand transfer transitions (d–d transitions) [20], we can assign the transitions at 460–545 nm in both the complexes as metal-to-ligand charge transfer (MLCT) transitions. However, metal-to-ligand charge transfer transition in complex (2) takes place at lower energy, i.e. 544 nm and with higher transition probability ($\varepsilon = 7030\ cm^{-1}\ M^{-1}$). This observation further substantiates the fact that due to extensive conjugation in catalyst (2) there is a strong transition probability for $p_{\pi^*} \leftarrow d_{\pi}$ resulting in less availability of unpaired electron in catalyst (2), thus reducing its performance to act as a chain transfer agent. These results of UV–vis absorptions are in agreement with previously reported values for catalysts (1) and (2) [14,21].

3.2. *Characterization of the polymer*

3.2.1. *Gel permeation chromatography*

The samples of PMMA were analysed on WATERS GPC 150C plus. The solvent was trichlorobenzene with column PL Gel 10 μm from polymer laboratories. The flow rate was 1.0 ml/min and temperature was 150 °C. Polystyrene standards were used for determining molecular weights and polydispersity of PMMA samples.

3.2.2. *NMR*

3.2.2.1. ^{1}H NMR. The ^{1}H NMR spectra for PMMA samples with 0.8% concentration were recorded on Jeol JNM-LA 500 NMR spectrometer at the frequency of 500 MHz at 25 °C. The ^{1}H NMR spectra were recorded with the following instrumental conditions: points = 32,768, sweep width = 10,000 Hz, scans = 16, solvent = $CDCl_3$.

The atactic PMMA formed in this work was verified, as reported in the literature previously [15,22,23], by the presence of $C–CH_3$ groups which produce three signals of very different intensities in the region 0.85–1.20 ppm in ^{1}H NMR. Chain transfer mechanism presented in Scheme 1 indicates that the resulting polymer $[P_n]$ should have vinyl protons. Absence of vinyl protons indicates that the termination is mainly taking place by coupling, while their presence indicates that termination is predominately taking place by disproportionation (because of chain transfer phenomenon) [24]. In order to see the vinyl protons of residual monomer and polymer, a magnification in the region of 5.4–6.2 ppm was performed (Fig. 2), which showed the presence of residual vinyl protons of polymer at 5.45 and 6.2 ppm. The position of these peaks remained unaffected with the changes in the molecular weight of the resulting PMMA.

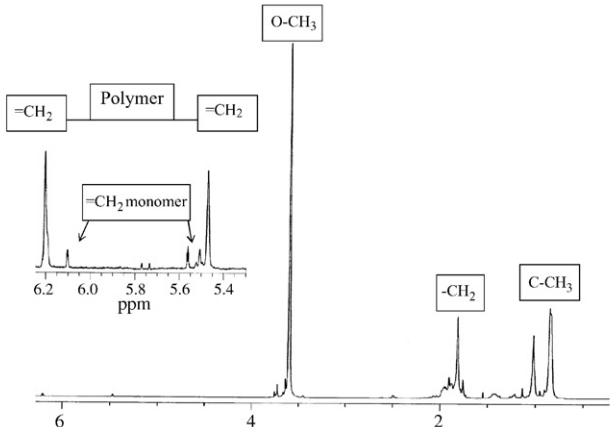


Fig. 2. ^{1}H NMR spectra of a representative PMMA with magnification from 5.4 to 6.2 ppm.

3.2.2.2. ^{13}C NMR and DEPT 135. The ^{13}C spectra were obtained at 125.65 MHz with ^{1}H broad band decoupling with 45° pulse angle. Other instrumental conditions were: points = 8192, sweep width = 33,003 Hz, solvent = $CDCl_3$, temperature = 25 °C. On the other hand, the DEPT 135 of 1% PMMA was recorded at 500 MHz with the following instrumental conditions: points = 65,536, PW1 = 7.80 s, PW2 = 16.80 μs, PW3 = 11.20 μs, temperature = 25 °C. For DEPT 45, PW1 = 7.80 s, PW2 = 5.6 μs, PW3 = 11.20 μs were used.

Although the ^{13}C spectra of PMMA is well known [25], we have recorded DEPT 135 to differentiate between $-OCH_3$ and methylene carbon atoms in the region 51.0–55.0 ppm, where both types of these C-atoms appear. The presence of methylene carbon atoms confirms the chain transfer phenomenon as described earlier. It was noted that two peaks around 54.20 and 54.38 ppm are inverted in DEPT 135 for all the samples polymerized by catalyst (1), thus confirming the presence of methylene-CH_2 (Fig. 3). Surprisingly, in DEPT 135, the

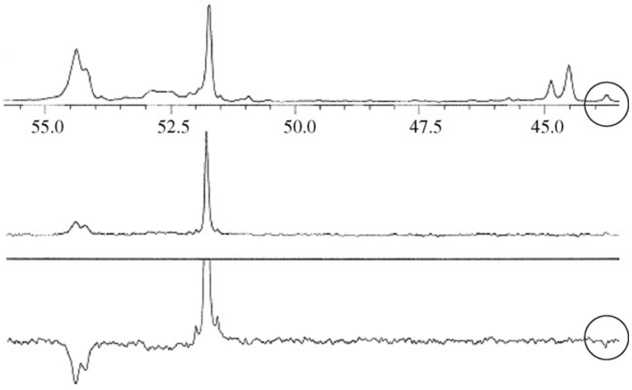


Fig. 3. ^{13}C NMR with DEPT 45 and 135 spectra of a representative PMMA sample.

carbon peak at 43.5 ppm was also inverted. This is possibly due to methylene carbons present at changeover position between isotactic and syndiotactic polymer.

3.3. Chain transfer constant (C_s)

The chain transfer constant C_s is represented as [26]

$$C_s = k_{tr}/k_p \tag{1}$$

where k_{tr} and k_p represent transfer rate constant (to chain transfer agent) and propagation rate constant, respectively. By an appropriate choice of polymerization conditions, one can determine the value of C_s [24] using the Mayo equation given below:

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_s\frac{[S]}{[M]} \tag{2}$$

where $1/DP_{n0}$ is the value of $1/DP_n$ in the absence of the chain transfer agent.

In the present work, percent conversion to polymer was kept under 8% for the PLP of MMA using catalyst (2) and below 16% for PLP of MMA by catalyst (1). For PLP of MMA in the presence of either of these two catalysts, there is a propensity for decrease in percent conversion to polymer with an increase in catalysts concentration but this decrease is not significant at higher catalyst concentrations as shown in Fig. 4. It is generally advisable to work below these percent conversions for better understanding of chain transfer phenomenon and also for a more precise calculation of the C_s value. In our case, however, somewhat higher percent conversion particularly with one of the catalysts was necessitated by the fact that the capacity of our quartz cell was only 4.0 ml and some reasonable amount of the polymer product was needed to carry out the characterization and other tests.

It is noteworthy that as in the case of other Co(II) catalysts reported this far [1,4,8,27,28], our catalysts are quite effective at ppm level. Initially, the number average molecular weight (M_n) was calculated with the help of ^{1}H NMR. The mole fraction of residual monomer was determined by the ratio of the area of the monomer vinyl proton peak around (6.10 ppm) to that of the vinyl peak due to the polymer around 6.21 ppm. The M_n of the polymer was determined by taking the ratio of the area (corrected for monomer) under the OCH_3 peaks (3.60 ppm) to that of the polymer vinyl peaks around (5.47 and 6.21 ppm). Extreme care was taken to minimize the integration error in determining the area under the peaks mentioned earlier. Previously [22,29], this technique was used to calculate the M_n for macronomers and it was found that the results were comparable to M_n values calculated from GPC.

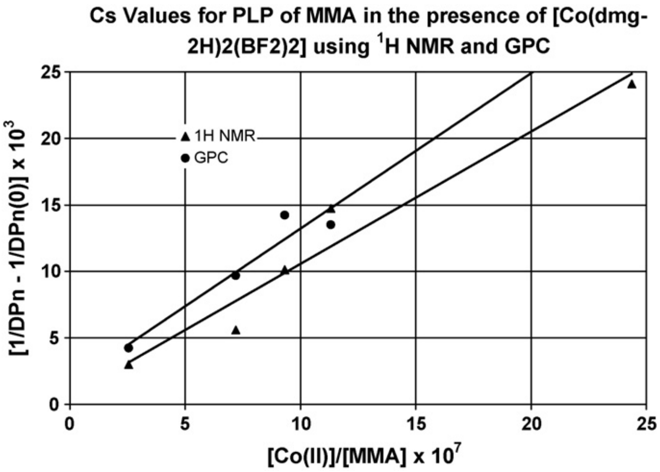


Fig. 5. Determination of chain transfer constant "C_s" value from ^{1}H NMR and GPC for PLP of MMA in the presence of $[Co(dmg\text{-}2H)_2(BF_2)_2]$ at 25 °C.

We note that there is a gradual decrease both on M_n and M_w values with an increase in catalyst (1) concentration (Figs. 5 and 6). A linear regression was performed on the experimental data in the form of $1/DP_n$ against [catalyst]/[MMA]. The slope of these lines passing through the origin gives the values of chain transfer constant (C_s) as 10,340 and 13,400 for number average molecular weights obtained from ^{1}H NMR and GPC techniques, respectively.

In our investigation, although the molecular weights determined from GPC results are different, as expected, from ^{1}H NMR, the trend of decrease in molecular weights is comparable and thus the "C_s" values calculated are in a reasonable agreement with each other, i.e. 13,400 and 10,340, respectively. The peak heights, although easier to measure, are not a reliable index

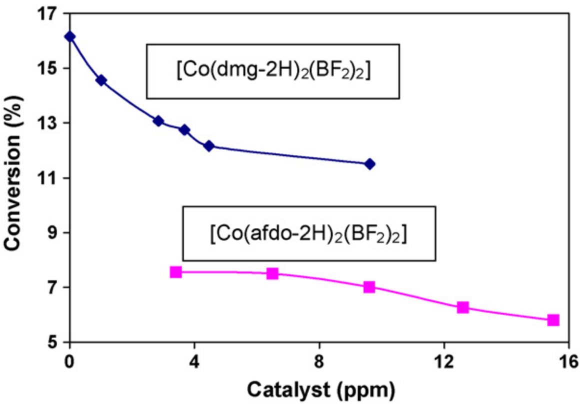


Fig. 4. Conversion (%) for pulsed laser polymerization of MMA using catalysts (1) and (2) at 25 °C.

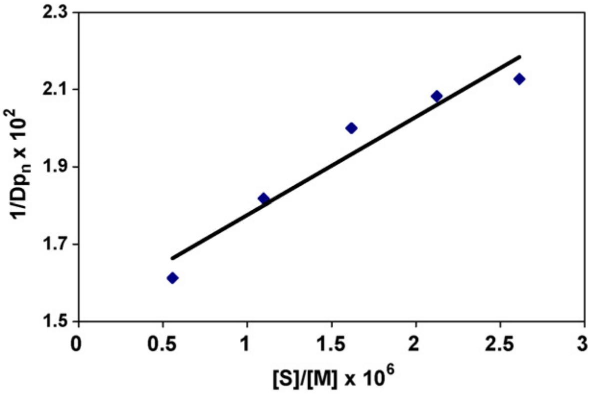


Fig. 6. Mayo plot for polymerization of MMA in the presence of $[Co(afdo\text{-}2H)_2(BF_2)_2]$ at 25 °C.

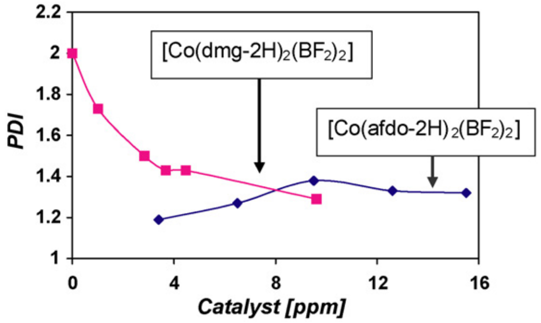


Fig. 7. Polydispersity index values for pulsed laser polymerization of MMA using $[Co(dmg\text{-}2H)_2(BF_2)_2]$ and $[Co(afdo\text{-}2H)_2(BF_2)_2]$.

of relative intensities [30], since peak widths, being proportional to T_2^{-1} (T_2 is spin–spin or transverse relaxation), will in general differ for different protons, and higher molecular weight of the polymer is expected from ^{1}H NMR technique.

For PLP of MMA by catalyst (2), the "C_s" value (Fig. 6) is a factor of 5 lower than the value found for the catalyst (1). Actually, cobalt(II) complexes are mainly of two types [31,32] and the unpaired electron in both types of paramagnetic complexes is believed to lie in the dz^2 orbital [33–35]. Therefore, Co(II) complexes are nucleophilic in nature, and hence, on the basis of the "C_s" values for catalysts (1) and (2), it is fair to conclude that the former has ostensibly more nucleophilic characters than the later. This is also supported from the spectroscopic data discussed later.

The polydispersity index (PDI) values are found to be lower than 2, especially with catalyst (2), as shown in Fig. 7. For catalyst (1), there is a gradual decrease in PDI values with concentration of the catalyst, which is consistent with earlier investigations [22,36] that report the following relationship:

$$v = 1/\{1 + C_s[S]/[M]\} \qquad (3)$$

Here, v is the probability of growth by addition of monomer to the growing chain, and [S] is the concentration of chain transfer agent. Therefore, increasing the concentration of chain transfer agent will decrease the polydispersity.

Pulsed laser polymerization of MMA in the presence of catalyst (2), however, has more "living radical polymerization" characters compared with catalyst (1). This suggests formation of a comparatively strong Co–C bond (Scheme 2) during the chain transfer process carried out by catalyst (1). The weaker Co–C bond formation for catalyst (2), on the other hand, may be due to the presence of electron-withdrawing furyl groups. Both these factors, i.e. weaker nuclephilic character but stronger $p_{\pi^*} \leftarrow d_{\pi}$ back bonding, reduce the availability of unpaired electron in dz^2 orbital in catalyst (2) to intercept the growing oligomer or polymeric chain. For catalyst (1), the dz^2 electron is at higher energy state because of substitution of $-CH_3$ groups in place of furyl groups. Not only the $p_{\pi^*} \leftarrow d_{\pi}$ back bonding is comparatively less in catalyst (1) due to loss of conjugation compared with the catalyst (2), but $-CH_3$ is also electron donating group due to the inductive effect or hyperconjugation. This makes higher energy for dz^2 orbital [37] which facilitates the interaction with the growing polymer chain (Rn). These observations are consistent with the free-radical polymerization of acrylates with Co(II) catalyst discussed by Wayland et al. [5,6]. The higher reversibility in Co–C bond formation with $[Co(afdo\text{-}2H)_2(BF_2)_2]$ catalyst may also be due to more steric repulsions due to the greater size of H_2afdo ligand than H_2dmg ligand in intermediate [LCo(III)Rn] (Scheme 2). This is in accord with previous observations of Wayland et al. [6] for the free radical polymerization of methyl methacrylate by cobalt (II) porphyrin complexes. They claimed that chain transfer catalysis is best achieved when there are minimal steric demands.

Our experimental observations showed that near the laser wavelength of 308 nm, the catalyst (2) had a molar absorptivity of 24,400 L mol^{-1} cm^{-1}, which is a factor of 4 higher than 5590 L mol^{-1} cm^{-1} measured for catalyst (1). This is also apparent from the laser light transmitted by the samples as shown in Table 1. The higher molar absorptivity may have two-fold effects. Firstly, the catalyst molecules (particularly catalyst (2)) in their excited states $[LCo(II)]^*$ may transfer their energy to monomer (MMA) or initiator (AIBN) and help in the initiation of photopolymerization.

$$[LCo(II)] + h\nu(\text{excimer laser photons}) \rightarrow [LCo(II)]^* \qquad (4)$$

$$[LCo(II)]^* + MMA/AIBN \rightarrow [LCo(II)] + (MMA/AIBN)^* \qquad (5)$$

Accordingly, there will be a certain radical formation from all those excited states created by the absorption of the laser light, and these could contribute to the polymerization process. How-

Table 1
Comparative results in the pulsed laser polymerization of MMA in the presence of $[Co(dmg\text{-}2H)_2(BF_2)_2]$ or $[Co(afdo\text{-}2H)_2\ (BF_2)_2]$ as chain transfer agent

Sample no.	[S]/[MMA] × 10^7 [a]		Transmitted energy (%)		Mn [b]		Mw [b]	
	$[Co(dmg\text{-}2H)_2(BF_2)_2]$	$[Co(afdo\text{-}2H)_2(BF_2)_2]$	$[Co(dmg\text{-}2H)_2(BF_2)_2]$	$[Co(afdo\text{-}2H)_2(BF_2)_2]$	$[Co(dmg\text{-}2H)_2(BF_2)_2]$	$[Co(afdo\text{-}2H)_2(BF_2)_2]$	$[Co(dmg\text{-}2H)_2(BF_2)_2]$	$[Co(afdo\text{-}2H)_2(BF_2)_2]$
1	–	–	79.1	79.1	9600		19200	
2	2.554	0.557	78.8	29.0	6800	6200	11800	7400
3	7.199	1.096	77.8	24.3	5000	5500	7500	7000
4	9.316	1.618	76.9	23.3	4100	5000	5800	6900
5	11.315	2.123	77.8	21.5	4200	4800	6000	6400
6	24.365	2.613	76.1	18.0	3200	4700	4100	6200

[a] [S] represents catalyst.
[b] The values have been rounded off to the nearest 100.

ever, in the present report, their relative contributions have not been measured. We intend to carry out further measurements in this direction and the findings will be reported in another paper. At the same time, as noted earlier, there is a decrease in both the molecular weights as well as percentage conversion of the polymers formed when any one of the two chain transfer catalysts is present. Furthermore, higher absorption of UV light by catalyst (2) suggests the possibility of facile Co–C bond breakage and as such, catalyst (2) is a comparatively weak chain transfer agent. In addition, possible chain transfer to initiator is also expected to be low since chain transfer constant C_s of catalyst (2) is 2530 while in the published literature (e.g., Principles of Polymerization by Odian [24]), chain transfer constant to initiator C_I of AIBN for the polymerization of MMA is only 0.02. Therefore, the overall contribution of the stronger absorption of laser light by catalyst (2) in enhancing the polymerization process is expected to be small.

On the other hand, our earlier study showed that without AIBN, the UV laser light at 308 nm did not generate any noticeable amount of free radicals and hence virtually no polymerization of MMA was observed. Therefore, AIBN is still the main initiator of polymerization.

As mentioned above, higher molar absorptivity by the catalyst molecules may contribute for facile Co–C bond dissociation, especially in catalyst (2). Absorption of UV photon of the proper wavelength can excite an electron due to which a strong δ-anti-bonding effect [38] would favor the breaking of Co–Rn in [LCo(III)Rn] intermediate. The four times higher tendency to absorb UV laser light at 308 nm for catalyst (2) compared to catalyst (1) results in strong δ-anti-bonding effect in Co–Rn bond for [LCo(III)Rn] intermediate of catalyst (2). This makes Co–Rn bond for catalyst (2) more fragile, and hence the equilibrium as shown in Scheme 2 will shift more to left hand side. This may be another reason for the lower C_s value of catalyst (2) compared to catalyst (1).

4. Conclusions

Chain transfer in pulsed laser polymerization of MMA using excimer laser (at 308 nm) with two different Co(II) catalysts as chain transfer agents has been investigated. We found that bis(boron difluorodimethylglyoximate) cobaltate(II) [Co(dmg-2H)$_2$(BF$_2$)$_2$] catalyst (1) is a better nucleophile than bis(boron difluorodialphafurilglyoximate) cobaltate(II) [Co(afdo-2H)$_2$(BF$_2$)$_2$] catalyst (2). Therefore, catalyst (1) acts as a superior chain transfer agent with higher C_s value of 13,400 than catalyst (2) with $C_s = 2530$. The observed living polymerization was dominant for catalyst (2) owing to weaker Co–C bond formation between growing polymer chain and the catalyst. The electronic spectroscopy (IR and UV–vis) reflects that there is a stronger back bonding in catalyst (2) than catalyst (1), thus hampering the ability of catalyst (2) to act as a strong chain transfer agent. The ^{1}H NMR shows that resulting PMMA is atactic in nature, while DEPT 135 indicates that peaks around 54.0 ppm are due to methylene C-atoms, thus indicating dominant chain transfer process.

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