Catalytic Chain Transfer in Crosslinking Photopolymerizations

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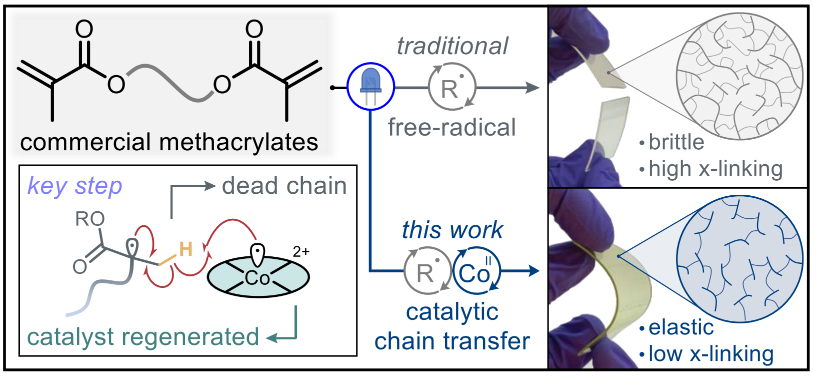
This paper is dedicated to Dr. Matthew McBride



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Abstract Presented here is a detailed account of the development and implementation of macrocyclic cobaloxime complexes as sulfur-free, catalytic chain transfer agents (CTAs) in crosslinking photopolymerizations. Although much of this review is dedicated to understanding the fundamentals of catalytic chain transfer (CCT) in photopolymerizations, its impact on network topology and resultant mechanical properties, future goals of applying this technology to multimaterial 3D printing are also discussed. It is our long-term ambition for catalytic, sulfur-free CTAs to supplant existing consumptive, sulfur-based agents to provide new, unexplored, and not currently possible to fabricate photopolymeric materials with a specific eye towards application in dentistry, additive manufacturing, and responsive materials.

Key words polymers, catalysis, photochemistry, chain transfer, cobalt

1 Introduction

We were late, stuck in Seattle rush hour traffic, and becoming increasingly aggravated by the situation. It was the summer of 2018, Dr. Matt McBride and I (B.T.W.) were taking part in the NSF I-Corps program under the guise of our nascent startup (Dynamic Matter, LLC). We were attempting to find a potential commercial application for work that we did based on covalent adaptable networks (CANs) in the Bowman lab at the University of Colorado-Boulder.[1–3] Professor A.J. Boydston (then at the University of Washington) had agreed to meet and talk about our technology, but this was dependent on getting to his office, ideally on time. We were late. Fortunately, Prof. Boydston, is an unflappably generous person, dismissed our apologies, even offering me a seltzer, which I gratefully accepted. During this meeting Prof. Boydston talked about work that was being done in his lab related to spatially resolved control over mechanical properties of stereolithographic parts using two different wavelengths of light (e.g. UV and visible).[4] He introduced the concept by saying, ‘wouldn't it be cool if you could 3D print a screwdriver from the same [resin] bath where the shaft and tip was glassy and the handle was rubbery?’ (**Figure 1**) I agreed that this would be very cool and, at the time, was an unaddressed market in photopolymer-based additive manufacturing with applications far beyond printing screwdrivers.

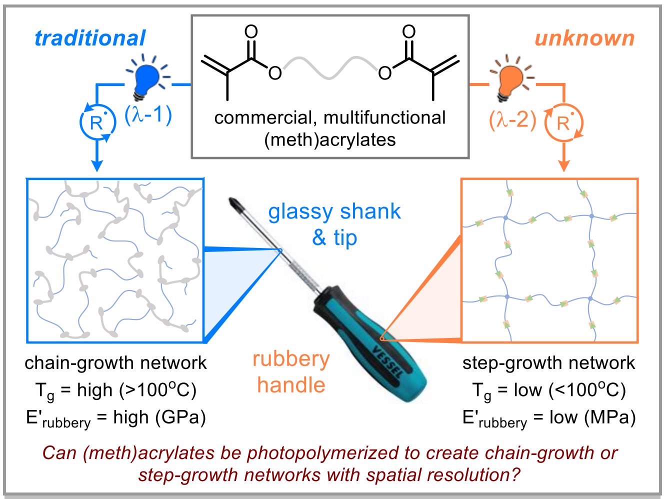


Figure 1 A traditional chain-growth free-radical polymerization of a multifunctional (meth)acrylate monomer can yield a glassy, highly crosslinked network, with mechanical properties resembling the shank and tip of a screwdriver. Here it is proposed that a step-growth free-radical polymerization of the same by an unknown mechanism would yield a rubbery, less crosslinked network, with mechanical properties resembling the elastomeric handle of a screwdriver.

On our drive back to the hotel and subsequent flight home, Dr. McBride and I discussed the concept of “multimaterials” at some length while sharing an Auntie Anne's pretzel (original flavor). We came to an agreement that the best and most commercially viable version of this would obey the following guidelines (**Figure 1**): 1) uses a single, ideally (meth)acrylate, polymerizable functional group to create both the hard (glassy) and soft (rubbery) materials, 2) uses commercial monomers that can be purchased inexpensively on large scales, 3) uses only photoinitiated, free-radical processes to create both the glassy and rubbery materials with good spatial resolution, and 4) the difference between the two materials (glassy and rubbery) would be created by a change in polymerization mechanism coupled to different wavelengths of light. Here, glassy materials are created by a traditional free-radical, chain-growth mechanism (λ-1, *UV light*) and the rubbery materials are created by a proposed, yet unknown, free-radical step-growth mechanism (λ-2, *visible light*). Regarding the final point (4), chain-networks are traditionally created during an uncontrolled free-radical photopolymerization of multifunctional (meth)acrylates. Chain-growth networks are usually extensively crosslinked, have a high, broad glass transition temperature (T_g >100°C), and a high modulus ($E'_{rubbery}$ >GPa). Comparatively, photopolymers prepared via a step-growth mechanism have a lower crosslinking density, have a sharp, lower glass transition temperature (T_g <100°C), and a lower modulus ($E'_{rubbery}$ < GPa).[5] In general, step-growth photopolymers are prepared using thiol-X chemistries (e.g. thiol-ene, thiol-Michael, thiol-epoxide).[6] To the best of our knowledge, there were no reports of a free-radical photopolymerization of (meth)acrylates that resulted in a step-growth network (**Figure 1**, *right*). Despite the lack of precedence, I still believe that this is a viable method for the on-scale production of spatially resolved multimaterials. We have, however, only begun work towards understanding how to synthesize (meth)acrylate-based photopolymers with a step-growth mechanism. We anticipate that this process will ultimately be controlled by a catalyst that can be switched ON or OFF with light to create different network topologies. Highlighted here are some stories, observations, and progress towards the development of a catalyst that can photopolymerize (meth)acrylates via a "step-growth"-like mechanism with spatial and temporal control.

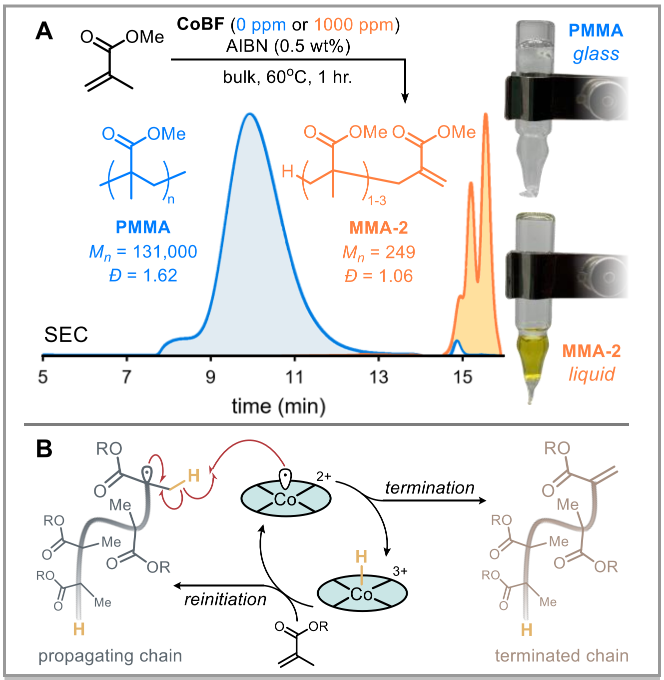


Figure 2 A. Recreation of the initial, accidental discovery of the catalytic chain transfer polymerization of methyl methacrylate (**MMA**). The bulk, thermal free radical polymerization of **MMA** created a glass consisting of high molecular weight **PMMA**, whereas in the presence of a cobalt catalyst (**CoBF**), only low molecular weight, liquid oligomers were formed. Ampoules shown are upside down to show differences in polymer phase (solid vs. liquid). **B.** The most current, widely accepted mechanism of CCT with methacrylate monomers.

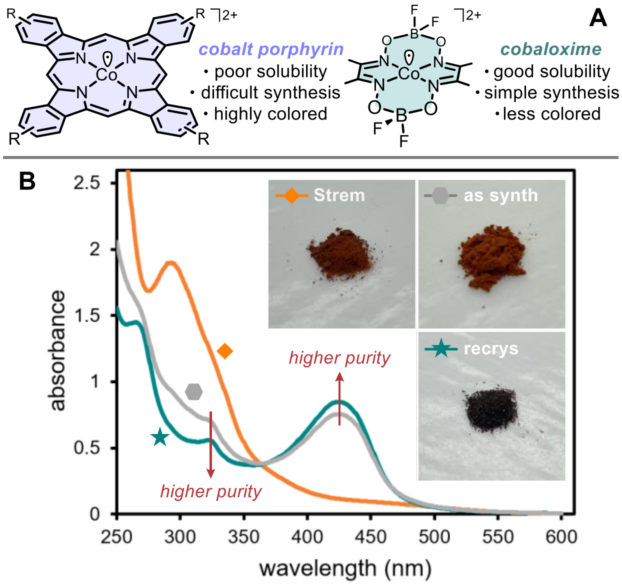
2 History of Catalytic Chain Transfer (CCT)

Although the seeds of this work were planted when I (B.T.W.) was a postdoctoral researcher, initial experiments were not addressed until I was an assistant professor at the University of Denver (DU) in the Department of Chemistry & Biochemistry. I am uncertain as to how I came across the excellent review "The 25th anniversary of catalytic chain transfer" by Alexei Gridnev,[7] but I recall reading it many times and was drawn to the simplicity and commercial relevancy of the work. Outside of the presented science, I also found the writing style, storytelling, and the accidental discovery of catalytic chain transfer (CCT) to be enthralling. I was drawn to a specific passage from this review that stated, "The very first experiments with cobalt porphyrin gave quite odd results. The [free radical] polymerization of [methyl methacrylate (**MMA**)] was complete, but the contents of the ampoule remained liquid." A recreation of this experiment and relevant size exclusion chromatography (SEC) results can be seen in **Figure 2A**. Those who have done a free-radical polymerization of **MMA** to high conversion know that **PMMA** will form a glass, not a liquid.[8] Subsequent research revealed that the cobalt species was acting as a very potent chain transfer agent (CTA), reducing the molecular weight of **PMMA** from many thousands of Daltons in the absence of cobalt (e.g. 131 kDa) to a mixture of liquid oligomers, which consisted primarily of an alkene terminated dimer (**MMA-2**, ~30%).[9] The presence of parts per million (ppm) of a cobalt catalyst effectively switches the polymerization mechanism from chain-growth to step growth, producing primarily dimer with high monomer conversions (>70%). In short, CCT was just what we were looking for (**Figure 1**, *left*).

The currently agreed upon mechanism for CCT, as seen in **Figure 2B**, proceeds by a hydrogen from the propagating polymer chain (*left*) being abstracted from the β-methyl by a low-spin, macrocyclic Co(II) complex.[10,11] This reaction forms an alkene-terminated polymer chain (*right*) and a presumed Co(III)-hydride species. The transient Co(III)-hydride is proposed to then undergo hydrogen atom addition to methacrylate monomer, starting the new chain and regenerating the catalytic Co(II) complex. Although other mechanisms have been proposed,[12] the pathway detailed in **Figure 2B** is supported by a strong isotope effect (k_H/k_D) of ~3.5, which is indicative of a hydrogen atom abstraction by a metalloradical,[13] as observed in other systems. It should be noted that this mechanism is currently widely accepted but still there is some debate regarding the structure and reactivity of the presumed cobalt(III) hydride.[14]

Since the discovery and optimization of CCT with cobalt(II)-complexes, this technology has been employed in a variety of academic and industrial applications, as reviewed in excellent accounts by Gridnev,[7,9] Haddleton,[12] and Heuts.[15] Primarily, CCT has been used in the literature to create low molecular weight linear polymers from monofunctional methacrylate-based monomers, however, several instances where CCT was used to create materials from difunctional methacrylate-based monomers can also be noted.[16–18] In one poignant example, Guan demonstrated that higher loadings of a macrocyclic cobaloxime catalyst (1000 ppm, 0.1 wt%) could regulate the thermal free-radical polymerization of ethylene glycol dimethacrylate (EGDMA) to form hyperbranched polymers as opposed to crosslinked thermosets.[19] It was shown that by controlling propagation and chain transfer with a cobalt-based CTA, gelation could be fully suppressed to form soluble polymer with high monomer conversion (up to 70%). Subsequent work by Haddleton and co-workers evidenced that this technique was applicable to other multifunctional methacrylate-based monomers (both di- and tri-functional), fully suppressing gelation to create soluble hyperbranched polymers.[20] We hypothesized that, if used in correct proportions and optimized towards a given photoinitiating system, the crosslinking density of the resultant photopolymer could be tunably reduced akin to what is done currently with state-of-the-art sulfur-based CTAs (e.g. thiols, β-allyl sulfones, etc.).[21–25] Conspicuously, before our recent publication on the matter, we could find no usage of cobalt-based CTAs being used to modulate the crosslinking density (XLD) of photopolymers.

The work reviewed below, which is largely detailed in our recent communication,[26] demonstrates that cobalt-based CTAs are remarkably potent (ppm loadings) in photopolymerizations of formulations consisting of methacrylate monomers. Photopolymers prepared with cobalt-based CTAs were found to have tunable glass transition temperatures (T_g), rubbery moduli ($E'_{rubbery}$), and stiffness. Looking forward, however, we have one major question that currently remains unanswered: *are cobalt-based CTA complexes the key to unlocking the free-radical step-growth polymerization of multifunctional methacrylates* (**Figure 1**, *right*)*?* Perhaps. However, much work, as detailed in the subsequent sections, is to be established before addressing this question.



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legend	CoBF	A_{425}	A_{322}	A_{425}/A_{322}	C_s
◆	commercial	0.117	1.315	0.089	44
⬢	as synth	0.906	0.685	1.06	2,271
★	recrys	0.872	0.594	1.51	9,524

Figure 3 **A.** Different classes of cobalt(II) complexes used in CCT. **B.** UV/vis spectra of **CoBF**: commercial, Strem Chemical (*orange line*, diamond), as synthesized (*grey line*, hexagon), after recrystallization from MeOH (*green line*, star) in MeCN (all at 2.00*10-4 M). **C.** Taking a ratio of the two absorbance bands resulted in a higher ratio after recrystallization which corresponded to a higher observed chain transfer coefficient (C_s) in the bulk thermal polymerization of MMA.

3 Understanding Catalyst Purity and Chain Transfer Activity

Although CCT was discovered in the late 1970s employing cobalt(II)-porphyrins (**Figure 3A**, *left*),[27] macrocyclic cobaloximes (**Figure 3A**, *right*), or those derived from the reaction of glyoximes with cobalt(II) salts, quickly became the most frequently utilized catalyst.[28] Outside of offering improved chain transfer activity (as ranked by relative chain transfer coefficient, C_s), cobaloximes also could be made scalably from inexpensive materials and had good solubility in various bulk methacrylates.[29] Accordingly, some of the first experiments in my lab concentrated on synthesizing these inorganic complexes. We prepared cobaloximes in the 3+ oxidation state with a halogen as an axial ligand (e.g. Br or Cl) with the assumption that the complex would be reduced *in situ* to the active 2+ oxidation state during photopolymerization.[30] Unfortunately, in our hands, these did not show any obvious activity in standard formulations of photopolymers (e.g. dodecane dimethacrylate, **DDMA**), even at high loadings (e.g. 1 mol% or 10,000 ppm). Intriguingly, Janowitz,[31,32] Haddleton[33] and others have shown that a bridging -BF_2- group between the glyoxime units, forming a compound nicknamed **CoBF** (N,N′,N′′,N′′′-tetrafluoro-diborato) bis[μ-(2,3)-butanedionedioximato)]cobalt(II)), can drastically improve stability and oxygen tolerance of the cobaloxime in the 2+ oxidation state. Despite the positives, determining the purity and activity of **CoBF** is historically challenging. Authors will normally use single batches of **CoBF** for an entire publishable study due to significant batch-to-batch catalyst variability.[33] We too ran into similar problems, quickly realizing that purity of the catalyst was directly proportional to activity and the **CoBF** that we were making wasn't very pure.

We were preparing **CoBF** using the standard method developed by Espenson and co-workers,[34,35] which was operationally simple but gave relatively low yields of the complex (15% overall). We were testing catalyst activity by placing varying amounts of **CoBF** into **MMA**, thermally polymerizing to a low conversion (<15%) and plotting the SEC data via a modification of the Mayo equation (**Equation 1**) to obtain C_s values, which was the slope of the resultant line.[36] Results were underwhelming and experimentally taxing. We frequently obtained catalysts that were many orders of magnitude less active than what was reported by O'Driscoll,[37] Haddleton,[33] Heuts[38] and others. We tried many different things, which included a Zoom pep talk from Prof. Haddleton, purchasing a commercial sample of **CoBF** from Strem Chemicals (more on that later), altering the synthetic procedures, recrystallization from various solvents, and everything else we could think of. Sometimes we would prepare batches of **CoBF** that showed good chain transfer activity, sometimes not. One thing was clear, we would need to develop an experimentally simple method of determining the activity of the catalyst spectroscopically.

$$\frac{1}{DP} = C_s * \frac{[CTA]}{[monomer]}$$

Equation 1 A modified version of the Mayo equation. Plotting relevant SEC data obtained by using different concentrations of a chain transfer agent (CTA) will create a line, whose slope is the chain transfer coefficient (C_s).

Sometime later, I came across a patent regarding the synthesis of **CoBF** that caught my attention, the only catch was that it was written in Mandarin.[39] After translating much of the patent, it became clear that the relative purity of **CoBF** could be determined using a UV/vis technique, whereby an increase in the ratio of the absorbance peak at 425 nm over the peak at 322 nm indicated a "purer" catalyst (**Figure 3B**). Equipped with this knowledge we began taking UV/vis spectra of various batches of **CoBF** and relating this to the C_s value obtained from the thermal polymerization of **MMA**. As noted in **Figure 3C**, as this ratio increased (0.089 to 1.51), the observed C_s value also increased. A commercial sample (obtained from Strem Chemical, $388/500 mg) was found to have no activity under similar reaction conditions, evidencing the difficulty of reproducing experiments with this catalyst. We have found this positive correlation to be consistent across many different batches of **CoBF** and can be used to determine relative, but not absolute, activity. In general, we found that **CoBF** recrystallized once from methanol (see supporting information of citation 20) had an A_{425}/A_{322} ratio >1.50 with good activity (C_s = ~10^3). We are uncertain if this spectroscopic ratio has an upper limit (>1.60?), but presumably further recrystallizations or chromatography could create a more highly active catalyst. Either way, we have established a spectroscopic method for *de novo* determination of activity that is reliable and experimentally simple.

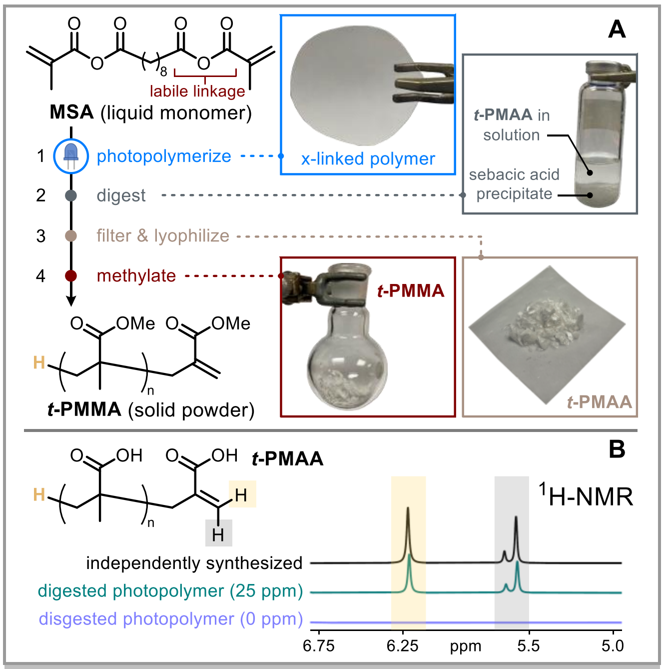

Figure 4 A. Workflow for determining the impact of a chain transfer agent (CTA) on a photopolymerization of a multifunctional methacrylate. First, methacrylated sebacic acid (MSA) is photopolymerized into a crosslinked polymer thin film (*blue box*) in the absence or presence of varying amounts of CTA which can be digested by refluxing in water. After cooling to room temperature, precipitated sebacic acid (*grey box*) can be removed by filtration and lyophilization of the supernatant yields an alkene-terminated poly(methacrylic acid) (*t*-PMAA, *brown box*). Exhaustive methylation of the polymer yields an alkene-terminated poly(methyl methacrylate (*t*-PMMA, *red box*) which can be analyzed by SEC. B. Overlayed NMRs of *t*-PMAA showing alkene termination of the polymer chain in the presence of CoBF (25 ppm, *green line*) and no alkene in the absence (0 ppm, *purple line*), compared to independently synthesized *t*-PMAA. The small peak at 5.64 ppm was presumed to arise from the isomerization of the alkene internally.

4 Evidencing CCT in a Crosslinking Photopolymerization

At this point we had made sufficiently pure **CoBF**, as determined by the bulk thermal polymerization of **MMA**, and now wanted to find a way to assess if this catalyst operated in a crosslinking photopolymerization. We were greatly inspired by a series of reports by Anseth and co-workers which detailed the use of a difunctional methacrylated sebacic acid (**MSA**) monomer,[40–42] which, when photopolymerized, formed crosslinked networks linked by hydrolytically unstable anhydrides (**Figure 4A**, *top left*). Accordingly, this monomer enabled the formation of crosslinked photopolymers which could be digested to form a linear poly(methacrylic acid) (**PMAA**) which was analyzable by SEC to give information regarding the molecular weight and dispersity of the internal polymer within a crosslinked network.[42] Building on this, we optimized the synthesis of **MSA** and the digestion protocol (**Figure 4A**). In short, the workflow consisted of photopolymerizing **MSA** to form a crosslinked photopolymer thin film which could be digested by refluxing in water. Upon cooling to room temperature, we found that the freed sebacic acid precipitated from the solution (due to its low solubility in water, 0.25 mg/mL) and could easily be filtered away.[43] Lyophilizing the aqueous supernatant yielded PMAA which could be exhaustively methylated to poly(methyl methacrylate) (**PMMA**) under standard protocols and analyzed by SEC.[44] When this workflow was done in the presence of **CoBF** (25 ppm), we noted the formation of an alkene peak in ^{1}H-NMR of **PMAA**, which we dubbed *terminated*-PMAA (***t*-PMAA**, **Figure 4B**). Comparing this to ***t*-PMAA** prepared by traditional, linear bulk CCT polymerizations,[45] we found matching alkene peaks (**Figure 4B**). Photopolymerizations done by a similar workflow, but in the absence of catalyst (0 ppm), evidenced no alkene formation. At this point we had confirmed that **CoBF** was acting as a catalytic CTA in the polymerization, but we needed to quantify specific activity.

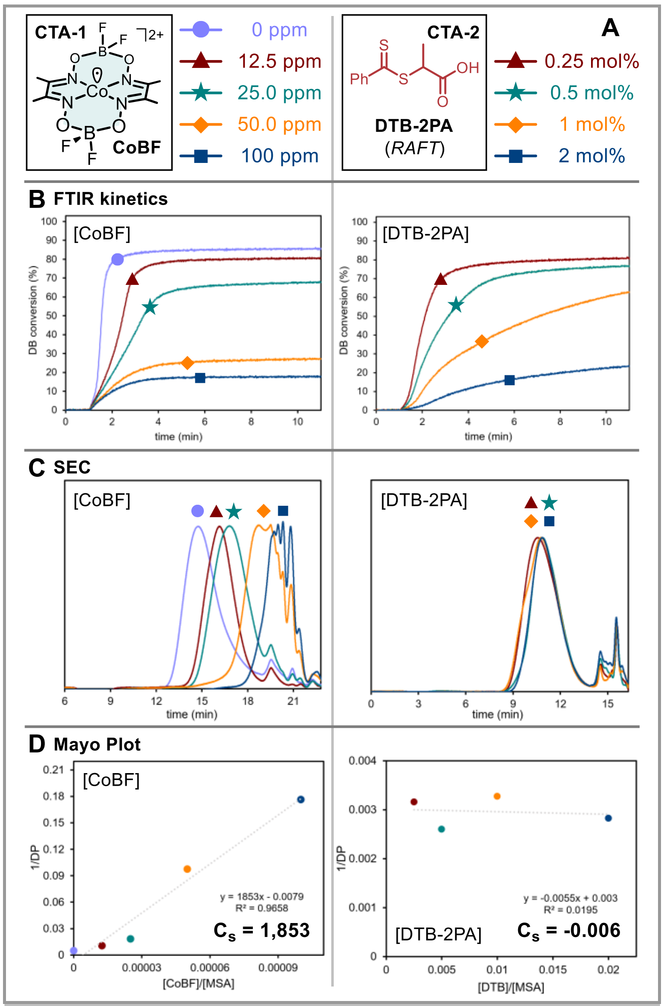

Figure 5 A. Two CTAs, CoBF and the RAFT agent DTB-2PA, were compared by the workflow outlined in Fig. 4A and the amounts that were added to the MSA resin (100 ppm = 0.01 mol%). B. FTIR kinetics for the photopolymerization of MSA in the presence of varying amounts of CTAs, showing a slowing of kinetics and reduced double bond (DB) conversion in both instances. Light (405 nm, 10 mW/cm^2) on at 1 min, continuously irradiated. C. Size exclusion chromatography (SEC) results showing a reduction of molecular weight of PMMA obtained by digestion of the photopolymer when CoBF was employed and similar molecular weight amongst samples when DTB-2PA was used. SEC in $CHCl_3$, PMMA standards. D. Mayo plots of SEC data showing strong chain transfer with CoBF (C_s = 1,853) and no obvious chain transfer with DTB-2PA (C_s = ~0); evidencing that kinetics and final DB conversion are not necessarily indicative of chain transfer.

5 Comparing Cobalt(II)-Catalysts to Other Relevant Chain Transfer Agents

With confirmation that **CoBF** was active in the photopolymerization of **MSA** (**Figure 4B**), we next needed to understand how active it was by determining its chain transfer coefficient (C_s). C_s values are unitless and can be used to benchmark the activity of different CTAs independent of mechanism of action, chemical structure, or the like.[46–48] Generally, C_s values are utilized to estimate the loading required to make an impact on the polymerization. For example, imagine if there were two different CTAs, specifically **CTA-1** and **CTA-2**; **CTA-1** has a C_s value of ~10^1 and **CTA-2** has a C_s value of ~10^3. Given this, **CTA-1** is ~1,000x less active in polymerization than **CTA-2**, all things held the same. If one were to replace **CTA-1** with **CTA-2**, an approximately 1,000x lower loading of **CTA-2** could be utilized while having similar impact on the molecular weight of the resultant polymer. C_s values are also simple to obtain experimentally. Generally speaking, 4-5 different polymerizations are run in the presence of varying concentrations of a CTA, the resulting SEC data is plotted according to **Equation 1**, and the slope of the linear regression is the C_s value. We have found that the Mayo equation can readily be applied to SEC data obtained from digestion of crosslinked photopolymers prepared from **MSA** (workflow detailed in **Figure 4A**).[26]

Although the workflow for determining a C_s value from a crosslinked photopolymer is experimentally taxing (**Figure 4A**), it is rigorous and necessary to directly compare CTAs. As an illustration we have selected two CTAs to compare as a case study, as detailed in **Figure 5**: **CoBF** and the reversible addition fragmentation chain transfer (RAFT) agent dithiobenzoate-2-propanoic acid (**DTB-2PA**).[49] First, different quantities of these CTAs were placed into **MSA**: 0-100 ppm for **CoBF** and 0.25-2 mol% for **DTB-2PA**, with a general note that 100 ppm = 0.01 mol% (**Figure 5A**). Nine separate samples were photopolymerized and the kinetics/double bond (DB) conversion as a function of time was tracked by FTIR (**Figure 5B**). As can be noted, both CTAs reduced the kinetics of the photopolymerization and the final DB conversion. As chain transfer reduces the rate of propagation (k_p) by providing a non-productive pathway for the free radical (k_{ct}), it is generally accepted that the addition of a CTA will retard kinetics.[50] Therefore, if viewing only the FTIR data, one could assume that both CTAs (**CoBF** and **DTB-2PA**) are reducing the molecular weight of the internal polymer chain of the network via chain transfer. However, after subjecting these 9 samples to the workflow described in **Figure 4** and analyzing the digested products by SEC (**Figure 5C**), one can note that increased loadings of **CoBF** resulted in significantly lower molecular weights of the polymer, whereas, **DTB-2PA** had no notable impact independent of loading. This is reflected in the Mayo plot (**Figure 5D**) where **CoBF** was a very active CTA (C_s = 10^3) and **DTB-2PA** evidenced no chain transfer activity (C_s = ~0). To summarize, we found that **CoBF** was an extremely potent CTA in the photopolymerization of methacrylate-based formulations. Further comparisons to other CTAs such as mercaptopropionic acid (C_s = 0.05) and the addition-fragmentation chain transfer (AFCT) agent beta-allyl sulfone (C_s = 0.12) showed that **CoBF** was 10,000-100,000 times more efficient than the best performing state-of-the-art CTA.[26]

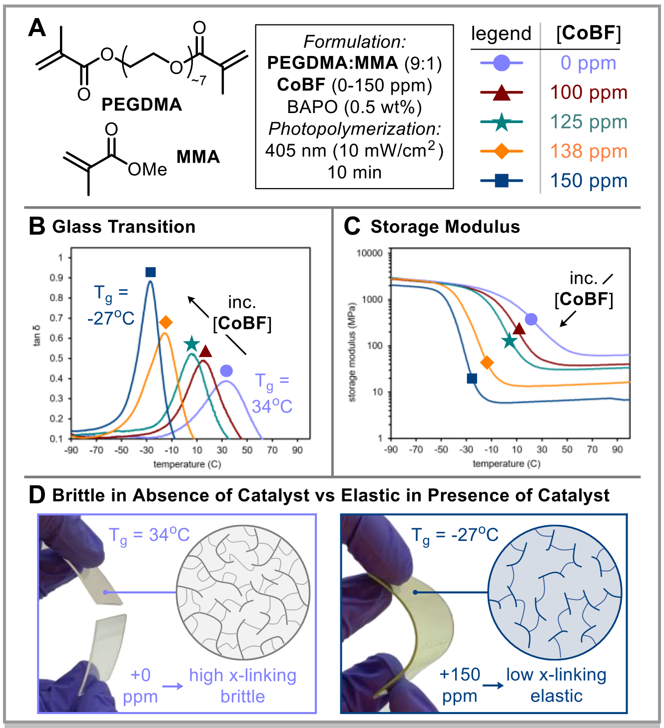

Figure 6 A. Thin films (1 mm) were prepared by photopolymerizing (405 nm, 10 mW/cm^2, 10 min) a formulation consisting of commercial monomers, PEGDMA (M_n = ~550) and MMA, in the presence of varying amounts of CoBF (0-150 ppm). B. *Tan δ* curves showing increased CoBF loadings result in photopolymers with lower and sharper glass transition temperatures (T_g). C. Storage modulus curves showing increased CoBF loadings result in a reduced modulus in the rubbery plateau, evidencing lower crosslinking density. D. A visual demonstration of mechanical differences between a photopolymer prepared in the absence of catalyst, which is brittle, and in the presence of catalyst (150 ppm), which is elastic.

6 Performance of Cobalt(II) Catalysts in Commercial Resins

We next sought to determine the impact of **CoBF** on the mechanical performance of photopolymers prepared using commercial monomers. To this end, varying quantities of **CoBF** (0-150 ppm) were added to formulations consisting of the commercial monomers poly(ethylene glycol dimethacrylate) (**PEGDMA**, M_n = ~550) and **MMA** and these samples were photopolymerized under relevant conditions (**Figure 6A**). Thermomechanical testing of these samples revealed that the addition of increasing concentrations of **CoBF** could tunably reduce the glass transition temperature (T_g) while creating more homogeneous networks (higher *tan δ*, sharper transitions, **Figure 6B**). The impact of **CoBF** on the mechanics was further illustrated by identifying the rubbery modulus ($E'_{rubbery}$), the storage modulus value at T_g,+50°C, which was found to be correspondingly lowered with increasing concentrations of **CoBF** indicating a reduction in crosslinking density (**Figure 6C**). The alteration of mechanical properties with this commercial material could also be noted visually, as shown in **Figure 6D**. Here, a photopolymer prepared in the absence of **CoBF** (0 ppm, *left*) was found to be highly crosslinked and brittle, which broke easily when bent. Alternatively, adding **CoBF** (150 ppm, *right*) to the same formulation created a photopolymer with significantly reduced crosslinking density that was elastic, bendable, and not easily broken.

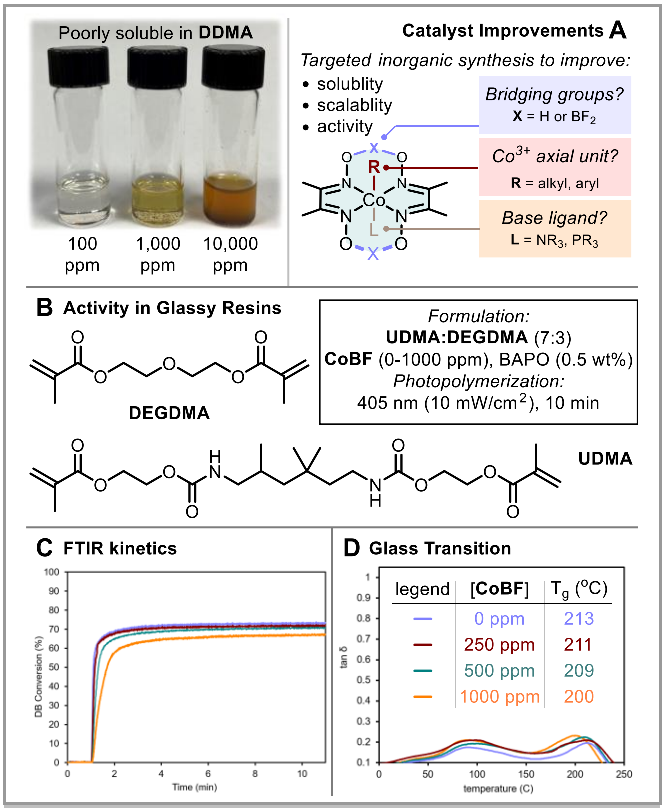

Figure 7 A. CoBF was found to have poor solubility in a variety of aliphatic resins, including dodecanedimethacrylate (DDMA, *left*). Future catalyst designs to be explored to increase the solubility, scalability, and activity of cobaloxime CTAs (*right*). B-D. When exploring the activity of CoBF (0-1000 ppm) in a formulation that would create a glassy material at room temperature (UDMA/DEGDMA, 7:3), greatly reduced chain transfer activity was observed when compared to formulations that create rubbery materials at room temperature (e.g. PEGDMA/MMA, Figure 6). FTIR kinetics remained similar (light on at 1 min, irradiated continuously, 405 nm, ~10 mW/cm^2) and glass transition temperatures (T_g) were similarly broad and only slightly reduced independent of catalyst loading.

7 Limitations of Approach and Looking Forward

CoBF has been shown to be an extremely potent catalyst in rubbery photopolymers, being many times more active than state-of-the-art consumptive CTAs (thiols, AFCT agents, etc.). Unfortunately, moving outside of PEG-based resins, we found that **CoBF** was poorly soluble in commonly utilized aliphatic monomers, such as dodecanedimethacrylate (**DDMA**). Additionally, although UV/vis techniques (**Figure 3A**) aided in determining the activity/purity of **CoBF**, its synthesis remains low yielding and operationally cumbersome. We, therefore, propose the targeted inorganic synthesis of various cobaloxime catalysts with the hope of improving its solubility in commercially relevant resins, making sufficient quantities (>5-gram batches), and ultimately producing a more active catalyst. We have the following questions that currently remain unanswered and must be addressed synthetically: 1) Are the -BF_2- bridging groups necessary? Can they be replaced with the synthetically simplified hydrogen bridge without compromising activity? 2) Can an organocobaloxime catalyst in the 3+ oxidation state be reduced *in situ* to form the active catalyst?[51,52] We hypothesize that this would improve the solubility and, as Co^{3+} is diamagnetic, would allow for direct determination of purity by ^{1}H-NMR. 3) Can base ligands improve activity and solubility? Historically several pyridine[53] and phosphine-based[54] ligands have been utilized, but their quantifiable impact on chain transfer activity remains sparce.

Finally, we have begun extending this approach to high-performance resins based on methacrylated-urethanes commonly utilized in dental materials and 3D printing resins,[24,55] such as urethane dimethacrylate (**UDMA**) blended with di(ethylene glycol) dimethacrylate (**DEGDMA**) to improve workability of the resin (**Figure 7B**). Strangely, even at what we consider a high catalyst loading of **CoBF** (1000 ppm), little retardation of rate was noted by FTIR (**Figure 7C**). Moreover, glass transitions (T_g) stayed multimodal with no sharpening of the transition and only minor shifts in the peaks (**Figure 7D**). Currently we do not have a strong understanding of why the catalyst is inactivated in glassy resins and exploring this effect will be the cornerstone of future work.

Looking forward, we plan to holistically explore the use of sulfur-free, catalytic CTAs based on cobalt complexes to improve and alter the mechanical properties of photopolymers. Despite many questions remaining unanswered, we believe that this catalyst could change the mechanism by which (meth)acrylates photopolymerize in the presence of free-radicals by introducing a competing, catalyst-controlled “step-growth”-like polymerization mechanism (**Figure 1**, *right*). We envision that many new, previously unexplored photopolymeric materials could be created just by adding small (ppm) quantities of this catalyst to commercial (meth)acrylate-based resins. Moreover, as the catalyst takes up little or no free volume in the resin, the positives of chain transfer (e.g. reduced shrinkage stress) can be realized without disrupting desirable secondary interactions between functional monomers (e.g. liquid crystals, urethanes, etc.), which is an issue with other consumptive sulfur-based CTAs (e.g. thiols, AFCT agents). Although long-term goals related to the 3D printing of multimaterials using catalytic methods remain unmet, we believe that understanding the fundamentals of this catalytic system is the key to unlocking its potential. As such, short-term goals will be related to answering underlying questions such as how to increase catalyst solubility/activity and obtaining good activity in high performance, glassy resins. Much of this work is already ongoing in our laboratory, so, if interested, please stay tuned.

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Conflict of Interest

The authors declare no conflict of interest.

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Biosketches

I was born and raised in Indianapolis, Indiana and have always been drawn to the natural sciences. Despite me being uncomfortably tall (6'11"), I never turned out to be much of a basketball player so perhaps a career in the sciences was fated. I attended undergraduate studies at Purdue University (West Lafayette, IN), graduate school at Scripps Research (La Jolla, CA), and did my postdoc at University of Colorado (Boulder, CO). Although I was formally trained as a synthetic organic chemist, my interests have wandered towards polymer chemistry and material science, as you can read about in this review. I started my independent academic career at the University of Denver in 2020 where we concentrate on making things that people can use and we will gladly pursue that wherever it takes us. Outside of work I can preferably be found eating, hiking, or skiing poorly with my wife, two young daughters, and our loveable mutt, Frankie.