Catalytic, Sulfur-Free Chain Transfer Agents that Alter the Mechanical Properties of Crosslinked Photopolymers

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ABSTRACT: Thermosetting materials generated by photopolymerization are inherently highly crosslinked and suffer from significant shrinkage stress, are often brittle, and have a limited range of mechanical properties. Various classes of chain transfer agents (CTAs) have been investigated and developed to reduce the crosslinking density of photopolymers by terminating kinetic chains and initiating new chains *in situ*. Although CTAs are successful in manipulating the mechanical properties of photopolymers, they are traditionally consumed during the polymerization and are therefore required in high loadings (up to 20 wt% of total formulation). Moreover, traditional CTAs frequently contain sulfur which is malodorous and can create unstable formulations. Presented here is a catalytic, sulfur-free CTA that can be added in ppm quantities to existing commercial monomer feedstocks to create photopolymers similar to those prepared using traditional CTAs, but at 10,000x lower loadings. These catalysts, which are based on macrocyclic cobaloximes, were found to tunably reduce the molecular weight of the kinetic chain proportional to catalyst loading. It was shown, using only commercial monomers, that this catalyst could reduce the glass transition temperature (T_g), rubbery modulus ($E'_{rubbery}$), and stiffness.

Thermosetting photopolymeric materials are most frequently fabricated from multifunctional (meth)acrylates via a free radical chain-growth polymerization.[1] Because photopolymers can be processed rapidly, in the absence of solvent, and often at room temperature, they have been identified as potentially green alternatives to traditional thermoplastic polymers.[2] To date, this class of materials has found widespread application as the polymer component in protective coatings, dental restoratives,[3] biomaterials,[4] 3D printed parts[5] and a growing list of other purposes. Despite their wide-spread utility, photopolymers are inherently highly crosslinked and suffer from significant polymerization induced shrinkage stress, offering practitioners access to only a limited window of mechanical properties. Many new chemistries, classes of designer monomers, and additives have been developed and investigated to mitigate these shortcomings,[6–11] however, to the best of our knowledge, no catalytic methods to reduce crosslinking density of a thermosetting photopolymer have been reported. Presented here is a catalytic method to effectively reduce crosslinking density of a photopolymer under standard, industrially relevant polymerization conditions (**Figure 1A**). This singular catalytic additive is highly potent (ppm quantities) and was found to reduce the glass transition temperature (T_g) and rubbery modulus ($E'_{rubbery}$) of a representative methacrylate-based photopolymeric resin proportional to catalyst loading. Investigation of degraded networks indicates that this catalyst operates by terminating the kinetic chain with an alkene, presumably through a metal-hydride intermediate (**Figure 1B**). We anticipate that given the low catalyst loadings required (over 99.99 wt% of the formulations were

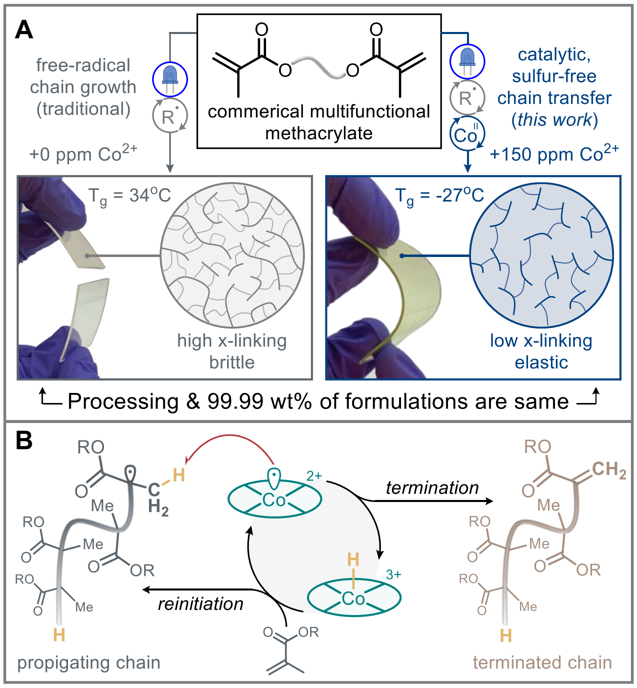
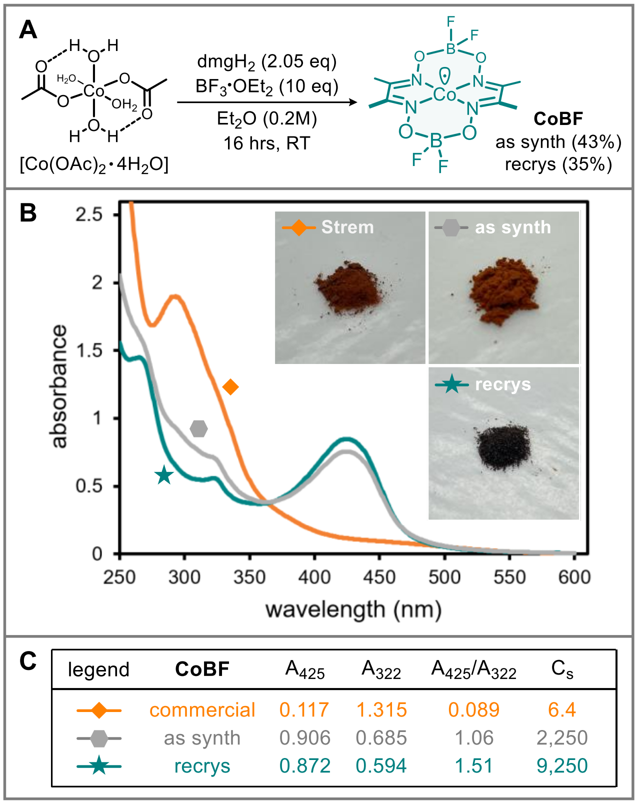


Figure 1: A. Free-radical chain growth photopolymerization leads to highly crosslinked, brittle polymers (*bottom left*), whereas catalytic, sulfur-free chain transfer photopolymerization leads to elastic photopolymers with low crosslinking (*bottom right*). **B.** Currently accepted mechanism of catalytic chain transfer of methacrylate-based polymers mediated by macrocyclic cobalt(II) complexes.

identical with and without catalyst) and realistic operating conditions, this catalytic chain transfer agent (CTA) could eventually supersede and supplant existing, consumptive sulfur-based CTAs currently used to modify the mechanical properties of crosslinked photopolymers. Presented here are our findings and initial work towards realizing these long-term goals.

In the realm of free-radical chemistry, CTAs are molecules that terminate a growing polymer chain and create a transient radical containing small molecule which subsequently creates a new polymer chain.[12] CTAs can, therefore, be used as sacrificial additives that proportionately reduce the length of the kinetic chain with increased concentrations. As sulfur is well-precedented in its capability of interacting with carbon-centered free-radicals, many classes of CTAs based around the sulfur atom have been developed.[13,14] Accordingly, sulfur-based CTAs are added to photopolymer formulations to alter and frequently improve their material and mechanical performance by beneficially reducing crosslinking density, delaying gelation, and precluding polymerization induced shrinkage stress. Photopolymers prepared in the presence of sulfur-based CTAs have been shown to create tougher materials, with higher elongation at break, and improved properties than those without. Unfortunately, high loadings (20-40 wt%) of these sacrificial CTAs must be added to formulations of multifunctional (meth)acrylates to achieve these benefits.[15,16] Moreover, many sulfur-containing CTAs can create unstable formulations when added to multifunctional (meth)acryaltes and/or require multi-step synthesis, reducing the viability and attractiveness of these materials in industrial applications.[17,18] As such, a catalytic, sulfur-free method to reduce crosslinking density of photopolymers would be of great utility, however, no such report can be noted.

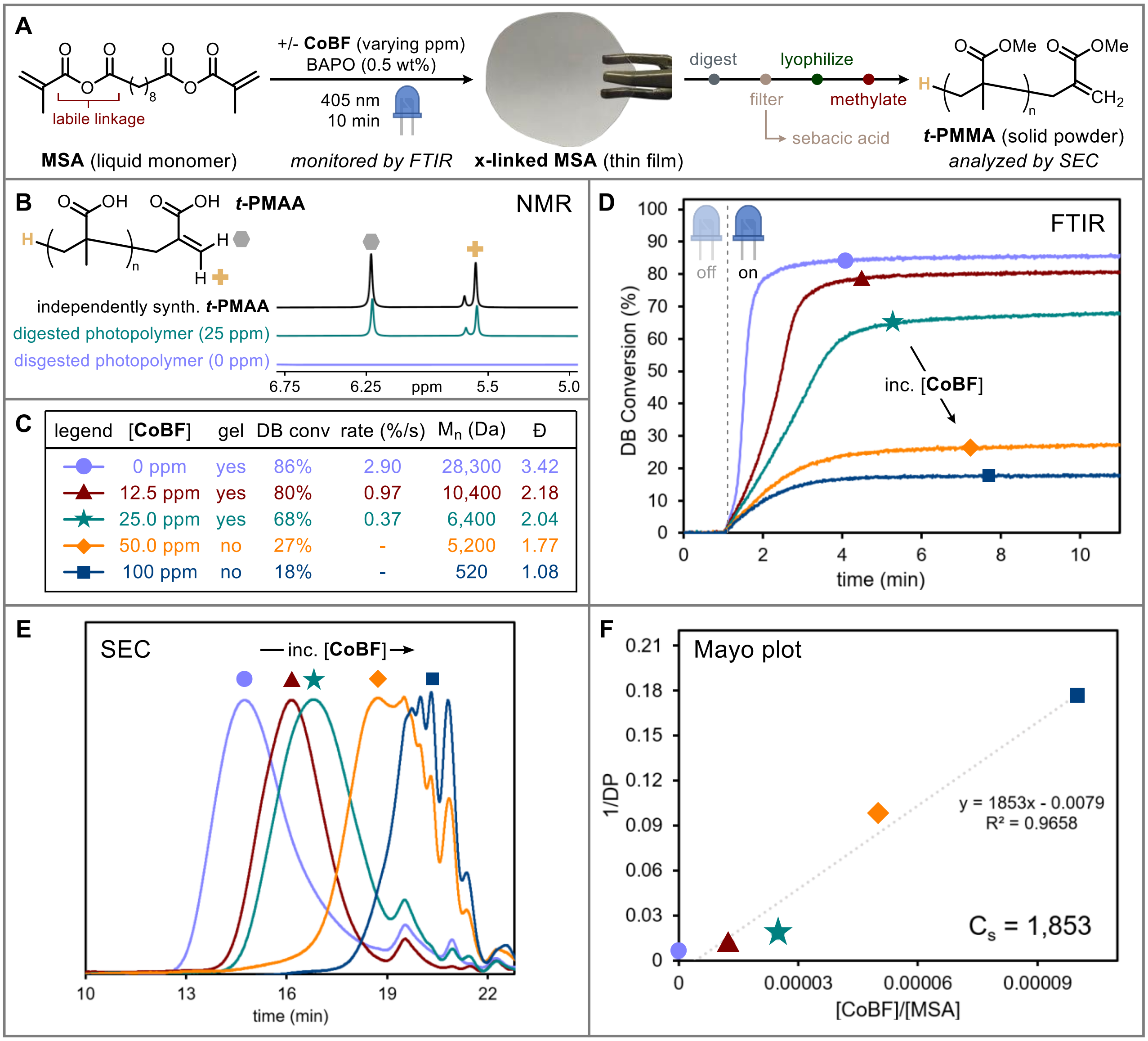
As the story goes, the capability of cobalt(II) complexes to catalytically reduce the molecular weight of linear polymers derived from methyl methacrylate (**MMA**) was discovered by accident.[19] Marchenko and co-workers were exploring the possibility for a cobalt(II)-porphyrin complex to act as a catalytic redox initiator. They were surprised to find that, although the polymerization reaction was complete by calorimetry, the contents of the ampoule remained liquid (high molecular weight poly(methyl methacrylate) [**PMMA**] would traditionally form a glass following polymerization). Subsequent research revealed that the liquid polymers were comprised of low molecular weight **PMMA** oligomers terminated with an alkene.[20] Although widely debated, the currently accepted mechanism of this process is shown in **Figure 1B**.[21] In short, a hydrogen from the propagating polymer chain (*left*) is abstracted from the β-methyl by the Co(II) complex to form a Co(III)-hydride and an alkene terminated polymer chain (*right*). The transient Co(III)-hydride is presumed to undergo hydrogen atom addition to methacrylate monomer, starting a new propagating chain and regenerating the active Co(II) catalyst.



legend	CoBF	A_{425}	A_{322}	A_{425}/A_{322}	C_s
◆	commercial	0.117	1.315	0.089	6.4
⬢	as synth	0.906	0.685	1.06	2,250
★	recrys	0.872	0.594	1.51	9,250

Figure 2: A. Synthesis of **CoBF** as described by Espenson. **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**.

Although many macrocyclic cobalt structures have been explored for their capacity to act as catalytic CTAs, cobaloximes with a bridging -BF_2- group between the glyoxime units, specifically **CoBF** (**Figure 2A**), have been shown to balance high chain transfer activity in the polymerization of mono-functional methacrylates, good solubility, and bench stability.[22] To this end, we purchased **CoBF** from Strem Chemical (100 mg/$96 USD) and synthesized it according to Espenson and co-workers (**Figure 2A**).[23,24] Unfortunately, we found that both commercial and synthesized **CoBF** had poor or inconsistent solubility in bulk monomers. Furthermore, as **CoBF** is paramagnetic, has few diagnostic protons and is colored, ascertaining the purity of this complex by NMR, mass spectrometry or visual inspection is historically challenging.[22] Alternatively, we found UV/vis to be a reliable method to determine the relative activity of **CoBF** (**Figure 2B**).[25] Specifically, it was observed in commercial samples of **CoBF** that absorption bands at 425 nm and 322 nm were not noted whereas freshly synthesized samples had strong bands at these wavelengths, which matched previously published reports.[23] Recrystallization of freshly synthesized **CoBF** from methanol yielded a microcrystalline dark red/brown solid with a slightly lower absorptivity at 322 nm, higher absorbance at 425 nm and excellent solubility in bulk monomers. Taking a ratio of the max intensity of the absorption bands (A_{425}/A_{322}) yielded a single, comparative numeric value. When these different catalysts were utilized to mediate the bulk thermal polymerization of methyl



legend	[CoBF]	gel	DB conv	rate (%/s)	M_n (Da)	Đ
●	0 ppm	yes	86%	2.90	28,300	3.42
▲	12.5 ppm	yes	80%	0.97	10,400	2.18
★	25.0 ppm	yes	68%	0.37	6,400	2.04
◆	50.0 ppm	no	27%	-	5,200	1.77
■	100 ppm	no	18%	-	520	1.08

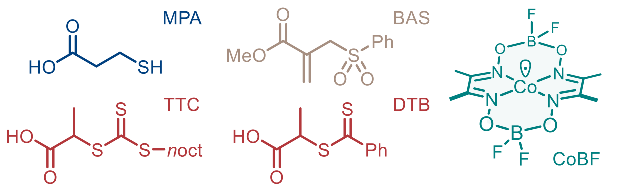
Figure 3: A. Photopolymerization of methacrylated sebacic acid (**MSA**) into a thin film which can be digested by refluxing in water. Removal of sebacic acid by filtration, lyophilization and exhaustive methlylation resulted in a alkene terminated poly(methyl methacrylate) (***t*-PMMA**) which is directly analyzable by NMR and SEC. **B.** Overlayed NMRs of ***t*-PMAA** showing alkene termination of the polymer chain in the presence of 25 ppm of **CoBF** and no alkene termination in the absence **CoBF**, compared to independently synthesized ***t*-PMAA**. **C.** Representative FTIR and SEC data showing the effect of **CoBF** loading on the polymerization. **D.** FTIR kinetic plot of the photopolymerization of **MSA** in the presence of varying loadings of **CoBF** (365 nm, ~10 mW/cm^2, light on at 1 minute and irradiated continuously). **E.** SEC plot showing the reduced kinetic chain length with increased loadings of **CoBF** ($CHCl_3$ eluent). **F.** A Mayo plot of SEC data. **CoBF** was calculated to have a chain transfer coefficient (C_s) of 10^3.

methacrylate (**MMA**), higher chain transfer coefficients (C_s) were obtained from catalysts with higher ratios (**Figure 2C**, see supporting information for more details).[26]

With a reliable method to produce highly active **CoBF** in hand, we next sought to explore the activity of this catalyst in the crosslinking photopolymerization of multifunctional methacrylates. We were interested to discover that Anseth and co-workers had previously developed a simple workflow to photopolymerize, degrade, and determine the kinetic chain length of polymers derived from hydrolytically unstable crosslinked thin films.[27–29] Given the simplicity and similarity of the photopolymerization conditions employed, we envisioned adapting this method to ascertain the effect of **CoBF** on crosslinking photopolymerizations. We noted some detractions, however, with Anseth's approach. First, despite the simple synthesis of their anhydride-linked dimethacrylate (methacrylated sebacic acid, **MSA**), in practice, we found this material contained large quantities of inseparable, methacrylate terminated oligomers which varied from batch to batch. Secondly, oligomeric **MSA** was a solid that needed to be heated to >60°C to be cast into a thin film, frequently resulting in premature gelation, yielding inconsistent results. Accordingly, we have devised a new synthetic route to **MSA** that yields a highly pure, well-defined, non-viscous, uncolored oil (see supplemental information). When properly stabilized (~1000 ppm of butylated hydroxytoluene [BHT]), **MSA** synthesized by this method is bench stable and >500 grams of this compound have been prepared to date.

The ability for cobalt(II) catalysts to alter the kinetic chain length and, therefore, reduce crosslinking density within crosslinked photopolymers was confirmed by the following workflow (**Figure 3A**): varying quantities of recrystallized **CoBF** (0 - 100 ppm) were added to **MSA** and this resin was photopolymerized to yield an anhydride crosslinked thin film under relevant conditions (0.5 wt% bis(2,4,6-trimethylbenzoyl)- phenylphosphineoxide [photoinitiator, **BAPO**], 365 nm, ~10 mW/cm^2, 10 minutes). These materials were then digested in refluxing water via hydrolysis of the anhydride linkage to form alkene *terminated*-poly(methacrylic acid) (***t*-PMAA**) and sebacic acid. Upon cooling the solution to room temperature, the sebacic acid was found to precipitate from solution and could be easily filtered away; the aqueous solution of ***t*-PMAA** was then lyophilized to form a free-flowing powder. Termination of the obtained ***t*-PMAA** with an alkene was confirmed by comparing ^{1}H-NMR spectra of the digested photopolymer prepared with 25 ppm of **CoBF** with a sample prepared independently by traditional catalytic chain transfer linear polymerization (see supporting information);[30] both samples showed identical protons in the vinylic region (**Figure 3B**). Notably, digested photopolymers prepared in the absence of **CoBF** (0 ppm) had no vinylic protons. Monitoring the kinetics of the photopolymerization by FTIR (**Figure 3C**) revealed that added **CoBF** delayed gelation at lower loadings (12.5 and 25 ppm) or fully inhibited gelation at higher loadings (50 and 100 ppm). It was also noted in all circumstances that double bond (DB) conversions were lower in the presence of **CoBF**, likely due to the formation of kinetic chains terminated with a DB that could not be differentiated from monomer (**Figure 3C-D**). Finally, the obtained ***t*-PMAA** was converted to alkene *terminated*-poly(methyl methacrylate) (***t*-PMMA**) via reaction with excess trimethylsilyldiazomethane ($TMSCH_2N_2$) and analyzed by size exclusion chromatography (SEC, $CHCl_3$ mobile phase).[31] It was discovered that low loadings (ppm quantities) of added **CoBF** could tunably and significantly reduce the degree of polymerization (DP) and dispersity ($Đ$) of the kinetic chain (**Figure 3D-E**). Lower loadings of **CoBF** (12.5 and 25 ppm) resulted in lower degrees of polymerization and dispersity when compared to a sample without **CoBF**. Alternatively, samples with higher loadings (50 and 100 ppm) of **CoBF** did not gel and consisted mostly of small oligomers. Treatment of this SEC data by plotting 1/DP versus [**CoBF**]/[MSA], as described by Haddleton and co-workers, yielded a Mayo plot which revealed a C_s value for recrystallized **CoBF** of 1,853 (**Figure 3F**).[26] Furthermore, **CoBF** was also shown to be highly active with other commercially relevant type I-photoinitiators and photopolymerization wavelengths (365, 405 and 470 nm, see supporting information).

Although **CoBF** is a highly active CTA in the photopolymerization of **MSA**, we were interested to explore how this catalyst performed when compared under similar conditions with other traditional sulfur-based CTAs. Accordingly, a mono-functional thiol (mercaptopropionic acid, **MPA**),[32–34] an addition-fragmentation agent (beta-allyl sulfone, **BAS**),[6] and two separate reversible-addition fragmentation chain transfer (RAFT) agents (trithiocarbonate, **TTC** and dithiobenzoate, **DTB**)[35] were added to **MSA** in varying quantities, photopolymerized, and submitted to a similar workflow as described above. Analysis of the data showed that **MPA** (entry 1) yielded high DB conversion (90%) but low C_s value (10^{-2}). Liska's addition-fragmentation reagent **BAS** (entry 2) was found to have similarly high DB conversions (84%) and a magnitude higher C_s values (10^{-1}). Interestingly, although the trithiocarbonate (**TTC**, entry 3) maintained high DB conversions, the dithiobenzoate (**DTB**, entry 4) was found to both slow the rate of polymerization and limit DB conversion, while both showed negligible chain transfer activity. Further mechanistic exploration of RAFT agents in photopolymers is ongoing. In agreement with studies detailed in **Figure 2**, **CoBF** from commercial sources (entry 5) or as synthesized by Espenson's procedure (entry 6) gave negligible or lower C_s values, respectively, when compared to **CoBF** recrystallized from methanol (entry 7). From these studies, it can be noted that **CoBF** acts as a very potent CTA in photopolymeric materials.

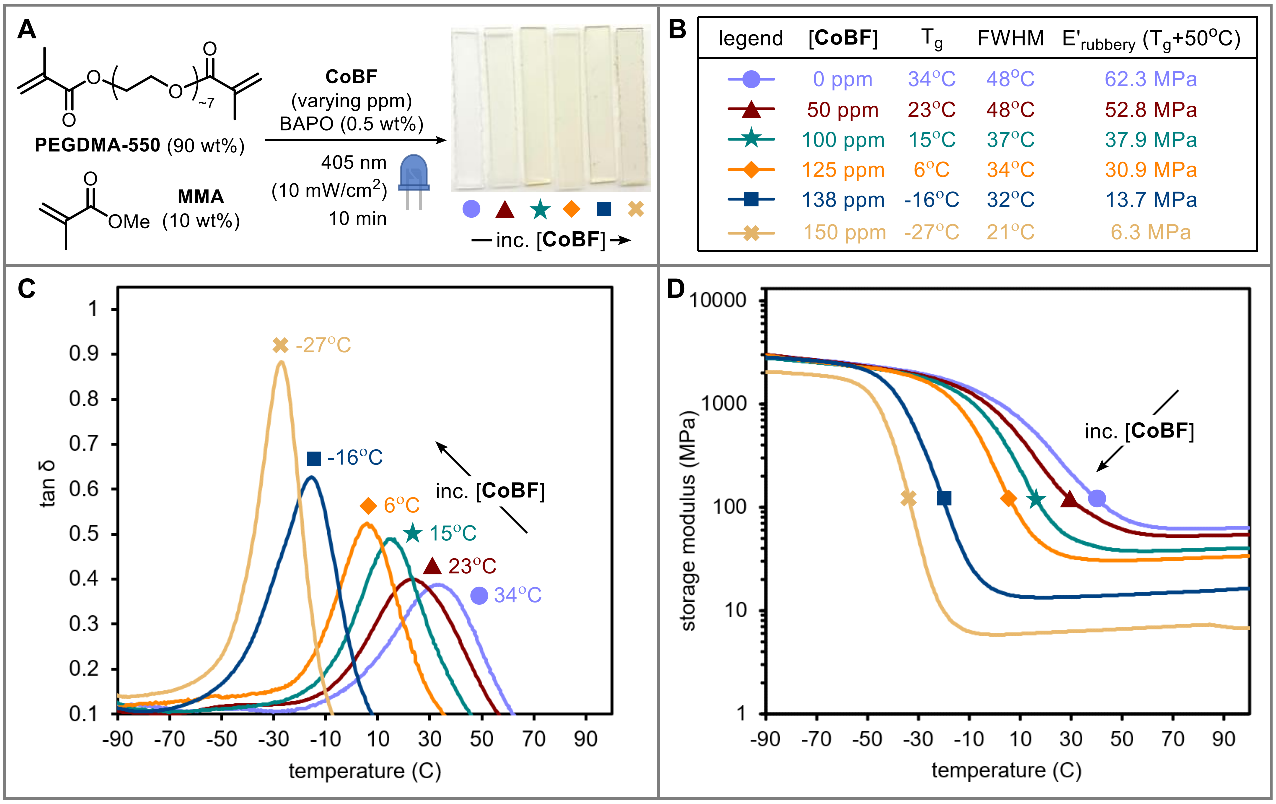


entry	CTA	amounts	avg DB conv	C_s
1	MPA	0.5, 1, 2, 4 mol%	90%	0.049
2	BAS	0.5, 1, 2, 4 mol%	84%	0.120
3	TTC	0.25, 0.5, 1, 2 mol%	92%	-0.039
4	DTB	0.25, 0.5, 1, 2 mol%	61%	-0.005
5	CoBF (Strem)	12.5, 25, 50, 100 ppm	83%	0.299
6	CoBF (synth)	12.5, 25, 50, 100 ppm	62%	306
7	CoBF (recrys)	12.5, 25, 50, 100 ppm	56%	1,853

***CoBF** is 10,000x more active than highest performing CTA*
(100 ppm = 0.01 mol%)

Figure 4: Structures of CTAs explored in the photopolymerization of **MSA** (*top*). Amounts of each CTA used to obtain data, average double bond conversion, and calculated C_s values (*bottom*).

We next investigated the effect of **CoBF** in methacrylate containing photopolymeric formulations derived from commercial monomers. Specifically, to formulations containing commercial poly(ethyleneglycol) dimethacrylate (**PEGDMA-550**, 90 wt%), **MMA** (10 wt%), and photoinitiator BAPO (0.5 wt%) were added varying ppm amounts of **CoBF** (0 - 150 ppm) and photopolymerized (405 nm, ~10 mW/cm^2, 10 min) under standard conditions (**Figure 5A**).[36] Submitting these samples to mechanical testing revealed that increased loadings of **CoBF** resulted in reduced and progressively sharp glass transition temperatures (T_g), which is indicative of more uniform networks being formed through chain transfer (**Figure 5B-C**). Moreover, as higher loadings of **CoBF** were employed, the rubbery modulus ($E'_{rubbery}$), which is determined by the modulus ~50°C above the T_g, was consistently found to be lower, indicating reduced crosslinking density.



legend	[CoBF]	T_g	FWHM	$E'_{rubbery}$ (T_g+50°C)
●	0 ppm	34°C	48°C	62.3 MPa
▲	50 ppm	23°C	48°C	52.8 MPa
★	100 ppm	15°C	37°C	37.9 MPa
◆	125 ppm	6°C	34°C	30.9 MPa
■	138 ppm	-16°C	32°C	13.7 MPa
✖	150 ppm	-27°C	21°C	6.3 MPa

Figure 5: A. Thin films were created by photopolymerizing (405 nm, ~10 mW/cm^2, 10 min) commercial monomers **PEGDMA-550** (90 wt%), **MMA** (10 wt%), photoinitiator BAPO (0.5 wt%) and varying ppm quantities of **CoBF** (0 – 175 ppm). Little color difference can be noted between samples prepared with the lowest (*left*) and highest (*right*) loadings of **CoBF**. **B.** Representative mechanical data of photopolymers prepared in the presence of **CoBF**. **C.** Tan delta curves showing increased **CoBF** loadings result in photopolymers with lower and sharper glass transition temperatures (T_g). **D.** Storage modulus curves showing increased **CoBF** loadings result in a reduced modulus in rubbery plateau.

It has been shown here that macrocyclic cobalt(II) complexes can act as potent CTAs in crosslinking photopolymerizations. Although this initial work indicates that such catalyst could open a vast formulation space for practitioners to explore, issues related to this catalyst retarding the rate of polymerization remains unresolved. Likely the addition of exogenous sigma-donating ligands, *in situ* reduction of macrocyclic cobalt(III) complexes to active catalysts, or using blends of monomers with orthogonal polymerization units (e.g. acrylates) will alleviate issues related to rate. This work, however, is ongoing in our laboratory. The impact of these catalysts to alter and improve the mechanical performance of commercially relevant photopolymeric materials used in dentistry and 3D printing resins will be explored in due course.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

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