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Communication

Catalytic, Sulfur-Free Chain Transfer Agents That Alter the Mechanical Properties of Cross-Linked Photopolymers

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ABSTRACT: Thermosetting materials generated by photopolymerization frequently 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 cross-linking density of photopolymers by terminating 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 the 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 10 000-fold lower loadings. These catalysts, which are based on macrocyclic cobaloximes, were found to tunably reduce the molecular weight of the 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 of a cross-linked photopolymer while utilizing identical processing conditions and keeping 99.99 wt % of the formulation the same.

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 thermoplastics.[2] To date, this class of materials has application in protective coatings, dental restoratives,[3] biomaterials,[4] 3D printed parts,[5] and others. Despite their utility, photopolymers offer practitioners access to only a limited window of mechanical properties. Accordingly, many new chemistries, classes of designer monomers, and additives have been developed and investigated to mitigate these shortcomings but are required in high loadings.[6−11] Although catalytic methods have been utilized in thermally activated thermosets,[12−14] no catalytic methods to reduce the cross-linking density (XLD) of a thermosetting photopolymer have been reported. Presented here is a catalytic method to effectively reduce the XLD of a photopolymer under standard, industrially relevant conditions (Figure 1A). This singular catalytic additive is 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. We anticipate that given the low catalyst loadings required (over 99.99 wt % of the formulations were 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 cross-linked photopolymers. Presented here are our findings and initial work toward 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.[15] CTAs can therefore be used as sacrificial additives that proportionately reduce the average molecular weight of the internal polymer chain. 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.[16,17] Photopolymers prepared in the presence of sulfur-based CTAs have been shown to create materials with improved mechanical properties compared to 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.[18,19] Moreover, many sulfur-containing CTAs can create unstable formulations when added to multifunctional (meth)acrylates and/or require multistep synthesis, reducing the viability and attractiveness of these materials in industrial applications.[20,21] As such, a catalytic, sulfur-free method to reduce the XLD of thermosetting photopolymers would be of great utility.

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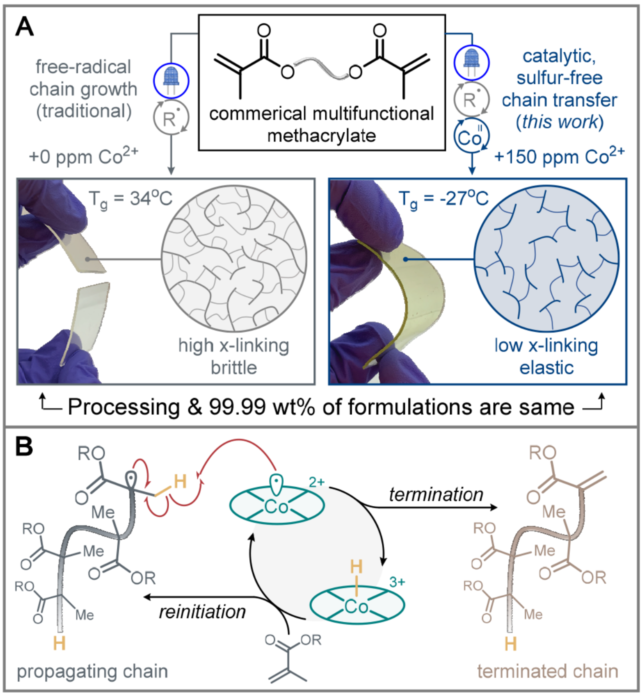


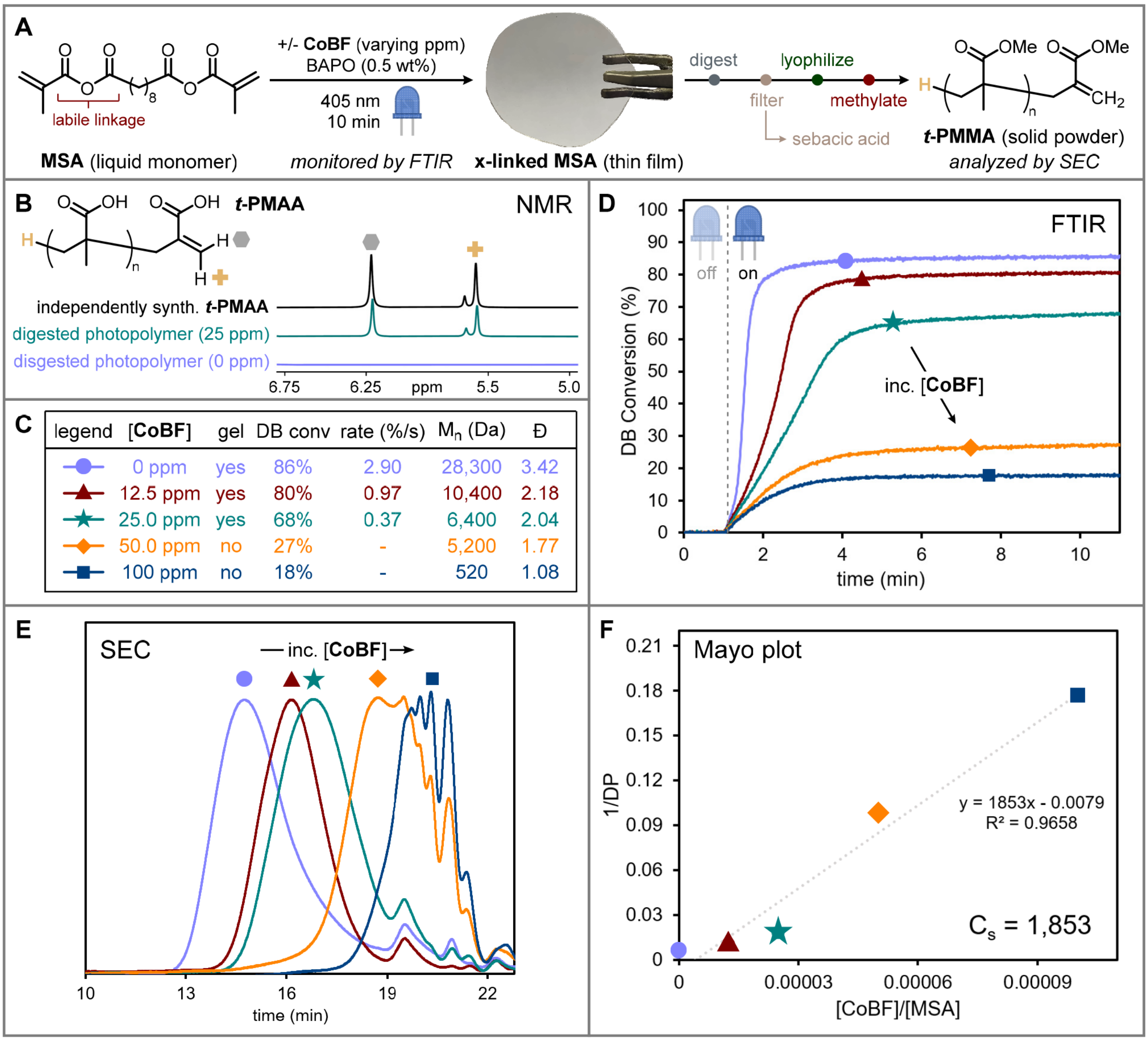
Figure 1. **A**. Free-radical chain growth photopolymerization leads to highly cross-linked, brittle polymers (*bottom left*), whereas catalytic, sulfur-free chain transfer photopolymerization leads to elastic photopolymers with low cross-linking (*bottom right*). **B**. Currently accepted mechanism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

The capability of cobalt(II) complexes to act as catalytical CTAs was reportedly discovered by accident.[22] When Enikolopyan 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 ampule remained liquid (high-molecular-weight poly(methyl methacrylate) [**PMMA**] would traditionally form a glass following polymerization). The liquid polymers were found to be composed of low-molecular-weight **PMMA** oligomers terminated with an alkene.[23] The currently accepted mechanism of this process is shown in Figure 1B.[24] 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.

Although many macrocyclic cobalt structures have been explored for their capacity to act as catalytic CTAs, cobaloximes[25,26] with a bridging $-BF_2-$ group between the glyoxime units, specifically **CoBF** (*N*,*N*′,*N*″,*N*‴-tetrafluorodiborato) bis[μ-(2,3)-butanedionedioximato)] cobalt(II)), have been shown to balance high chain-transfer activity, good solubility, and bench stability.[27,28] Despite this, determining the purity and activity of **CoBF** as a catalytic CTA is historically challenging. To this end, we have developed a simple spectroscopic technique to reliably assess the activity of a given batch or source of **CoBF** by matching to chain transfer coefficients (C_s values) obtained from the thermal polymerization of methyl methacrylate (**MMA**) to a ratio obtained from two absorption bands in the UV/vis spectra (see section 2.7 in the Supporting Information). Using this technique, different batches of **CoBF** can be benchmarked against each other spectroscopically.

We next sought to explore the activity of **CoBF** in the cross-linking 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 molecular weight of polymers derived from hydrolytically unstable cross-linked thin films.[29−31] Accordingly, we have devised a new synthetic route to Anseth's cross-linker **MSA** (methacrylated sebacic acid) that yields a nonviscous, uncolored oil (see section 2.2 in the Supporting Information). **MSA** synthesized by this method is bench-stable, and >500 g of this compound has been prepared to date. The ability of cobalt(II) catalysts to reduce XLD within cross-linked photopolymers was confirmed by the following workflow (Figure 2A): varying quantities of recrystallized **CoBF** (0−100 ppm) were added to **MSA**, and this resin was photopolymerized to yield an anhydride cross-linked thin film under relevant conditions (0.5 wt % bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide [photoinitiator, **BAPO**], 365 nm, ∼10 mW/cm^2, 10 min). 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; 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 ^1H 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 section 2.10 in the Supporting Information);[32] both samples showed identical protons in the vinylic region (Figure 2B). Notably, digested photopolymers prepared in the absence of **CoBF** (0 ppm) had no vinylic protons. Monitoring the kinetics of the photopolymerization by FTIR (Figure 2C) 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 chains terminated with a DB that could not be differentiated from monomer (Figure 2**C**−**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).[33] 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 internal polymer (Figure 2D,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 1853 (Figure 2F).[34] Furthermore, **CoBF** was also shown to be highly active with other commercially relevant

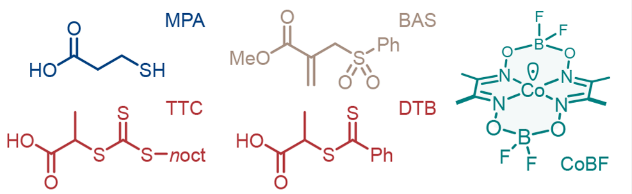


legend	[CoBF]	gel	DB conv	rate (%/s)	M_n (Da)	Đ
●	0 ppm	yes	86%	2.90	28,300	3.42
▲	12.5 ppm	yes	80%	0.97	10,400	2.18
★	25.0 ppm	yes	68%	0.37	6,400	2.04
◆	50.0 ppm	no	27%	-	5,200	1.77
■	100 ppm	no	18%	-	520	1.08

Figure 2. 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 **CoBF** and no alkene termination in the absence **CoBF**, compared to independently synthesized ***t*-PMAA**. The small peak at 5.64 ppm was presumed to arise from the isomerization of the alkene internally. **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 min and irradiated continuously). **E.** SEC plot showing reduced molecular weight with increased loadings of **CoBF**. **F.** Mayo plot of SEC data. **CoBF** was calculated to have a chain transfer coefficient (C_s) of 10^3.

type I-photoinitiators and photopolymerization wavelengths (see section 5.3 in the 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 monofunctional thiol (mercaptopropionic acid, **MPA**),[35−37] an addition−fragmentation agent (*β*-allyl sulfone, **BAS**),[6] and two separate reversible addition−fragmentation chain transfer (RAFT) agents (trithiocarbonate, **TTC** and dithiobenzoate, **DTB**)[38] were added to **MSA** in varying quantities, photopolymerized, and submitted to a similar workflow as described above. An analysis of the data showed that **MPA** (entry 1) yielded a high DB conversion (90%) but a low C_s value (10^{-2}). Liska's addition−fragmentation reagent **BAS** (entry 2) was found to have similarly high DB conversions (84%) and 1 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. **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 sufficiently pure **CoBF** acts as a potent catalytic CTA in photopolymeric materials.



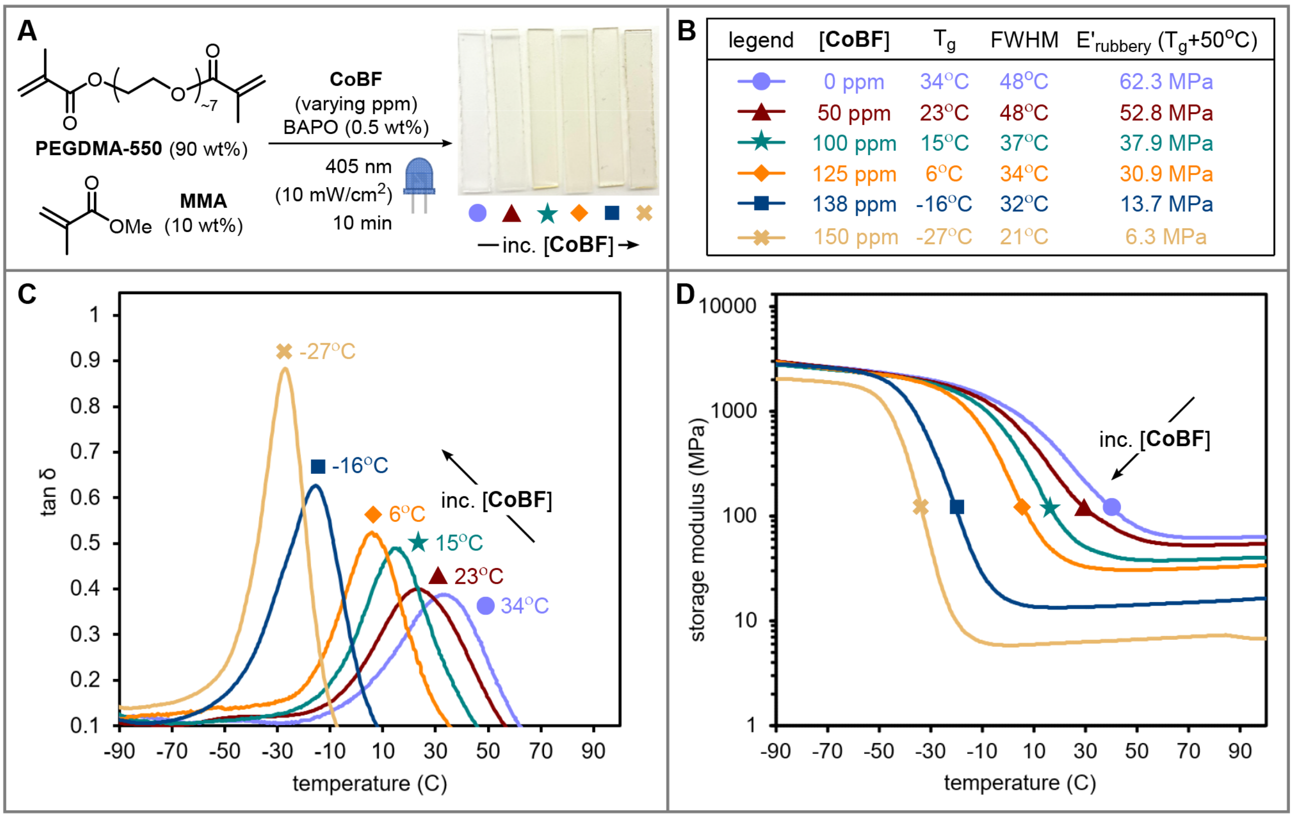
entry	CTA	amounts	avg DB conv	C_s
1	MPA	0.5, 1, 2, 4 mol%	90%	0.049
2	BAS	0.5, 1, 2, 4 mol%	84%	0.120
3	TTC	0.25, 0.5, 1, 2 mol%	92%	-0.039
4	DTB	0.25, 0.5, 1, 2 mol%	61%	-0.005
5	CoBF (Strem)	12.5, 25, 50, 100 ppm	83%	0.299
6	CoBF (synth)	12.5, 25, 50, 100 ppm	62%	306
7	CoBF (recrys)	12.5, 25, 50, 100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

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

Figure 3. 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(ethylene glycol) dimethacrylate (**PEGDMA-550**, 90 wt %), **MMA** (10 wt %), and photoinitiator BAPO (0.5 wt %) were added varying amounts of **CoBF** (0−150 ppm), following by photopolymerization (405 nm, ∼10 mW/cm^2, 10 min) under standard conditions (Figure 4A).[39] 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 4**B**,**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 XLD.

It has been shown here that macrocyclic cobalt(II) complexes can act as potent CTAs in cross-linking photopolymerizations. Although this initial work indicates that such a 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 σ-donating ligands,[26] the *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.



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 4. 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 δ 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 the rubbery plateau.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c03811.

NMR spectra for all compounds, additional experimental details, materials, and methods including photographs of experimental setups where necessary (PDF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent on this work has been submitted.

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