Catalytic Chain Transfer in Free-Radical Polymerizations

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1. General Features of Catalytic Chain Transfer

1.1. Free-Radical Polymerization

While free-radical chain reactions were known shortly after the turn of the 20th century, it was not until the mid-1930s that free-radical polymerization was recognized. Today, free-radical polymerization finds application in the synthesis of many important classes of polymers including those based upon methacrylates, styrene, chloroprene, acrylonitrile, ethylene, and the many copolymers of these vinyl monomers. Many good reviews and books on this subject are available.[1,2]

Free-radical polymerizations are subject to the many complications one might expect of radical chemistry, but the simple underlying mechanism is composed of three primary processes—*initiation*, *propagation*, and *termination*. Generally, the *initiation* takes place by cleavage of an azo or peroxide compound (the "initiator") to yield the "primary radical". In this paper, the chemistry will be limited to azo initiators because peroxides interfere with subsequent chemistry (see section 3.7). The *propagation* or growth reaction occurs when monomers add to the primary radical or to the radical at the end of the growing polymer chain. *Termination* occurs primarily by the bimolecular reaction of two growing polymer radicals. The two primary mechanisms observed are radical−radical combination and disproportionation in which one radical abstracts a hydrogen atom from another radical resulting in one saturated chain end and one olefinic chain end. In addition to these primary reactions, there are a variety of other reactions that occur. There may be very low levels of *chain transfer* to monomer, a reaction that leads to termination of one chain with simultaneous initiation of another new chain so that there is no change in the number of radical species present.

The propagation reaction in free-radical polymerizations is rapid.[1] One important feature of the polymerization is that high molecular weight polymer is formed even at very low levels of monomer conversion. Thus, each propagating radical or its progeny lives for well under a minute. To control molecular weights in these polymerizations, the use of chain

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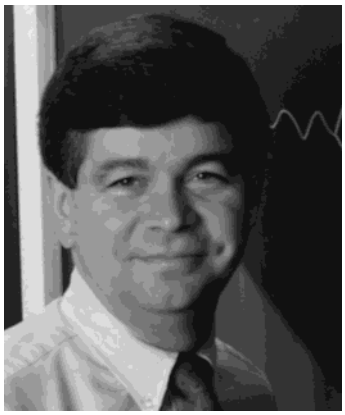
Alexei Gridnev graduated with his Masters degree from Moscow University of Fine Chemical Technology, Russia, in 1979 with majors in synthesis and technology of biologically active compounds. The same year he was employed by the Semenov Institute of Chemical Physics of the Russian Academy of Sciences, where he studied catalysis of chain transfer to monomer. In 1984 he received his Doctorate degree in Polymer Science. In 1986 Dr. Gridnev was transferred to the Institute of Physico-Technical Research of the Russian Academy of Sciences as a senior research chemist to work on several projects including the synthesis of model compounds for biochemical research. In 1992 he moved to the University of Pennsylvania in the laboratory of Professor Brad Wayland, where he continued the study of hydrogen transfer in reactions of free radicals with cobalt chelates as a senior research associate. In 1994 he began work for E.I. DuPont de Nemours and Co., first in CR&D in Wilmington, DE, and later at Marshall Laboratory in Philadelphia, PA. Alexei Gridnev is the author of more than 50 articles and patents, predominantly in the area of catalysis of free-radical processes.



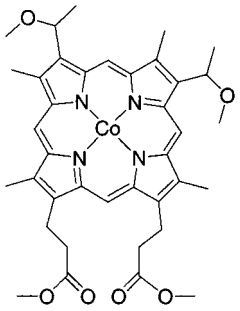
Steve Ittel was born in Hamilton, OH (1946), and received his B.S. degree in Chemistry from Miami University in 1968. After two years of studying photochemical smog in the greater New York City area for the USPHS, he attended Northwestern University, where he received his Ph.D. degree in Inorganic Chemistry in 1974 with Jim Ibers. Joining DuPont's Central Research, he was involved in the elucidation of fluxional processes in five- and seven-coordinate inorganic complexes. After work on C–H activation, diamagnetic and paramagnetic agostic M–H–C interactions, and cyclohexane oxidation, he moved to research management. Never straying far from the scientific edge, he has been involved in small molecule catalysis including hydrocarbon oxidation, fluoro-organometallic chemistry, and olefin hydrocyanation. The molecules started getting larger as his interests turned toward elastomeric polypropylene, catalytic chain transfer in free-free-radical radical polymerizations, and most recently ethylene polymerization with polar comonomers. He has over 100 publications and patents and a book to his credit. Another interest, having both technical and aesthetic aspects, is the nurture and styling of a collection of about 100 bonsai.

terminators is often employed.[3] Thus, compounds such as thiols will react with a growing polymer chain to yield a thiol-terminated species.[4,5] In this instance, there would be only one polymer chain per initiating radical and each polymer chain would be terminated stoichiometrically by one thiol. This approach is acceptable for moderate molecular weights but becomes problematic for the synthesis of very low molecular weight species.

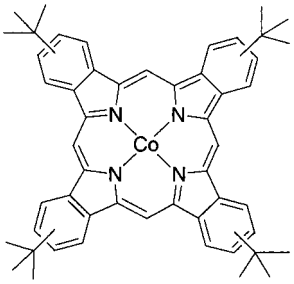
In general, radical reactions are not selective. The polymerizations allow only a limited degree of control. For instance, tacticity of the polymerization may be controlled by the addition of Lewis acids.[6] The reactivity ratios of monomers and rates of polymerization can also be controlled by the addition of Lewis acids.[7−9]

1.2. Catalytic Chain Transfer

In 1975, Boris Smirnov and Alexander Marchenko discovered a method in which they could control the molecular weight in a methacrylate polymerization by introducing catalysts that could greatly enhance the process of chain transfer to monomer.[10] They found that substituted cobalt porphyrins, **1**, or benzoporphyrins, **2**, provided dramatic reductions in the molecular weight of the methacrylate polymers during radical polymerization with little to no reduction in overall yield of polymer.[11−15]



1, cobalt tetramethoxy hematoporphyrin-IX



2, cobalt tetra-(*tert*-butylbenzo)porphyrin

The catalytic chain-transfer (CCT) process displays all of the features characteristic of typical, uncatalyzed chain transfer other than taking place at a rate competitive with chain propagation. Thus, the rate of polymerization at low conversions is independent of the concentration of the cobalt porphyrin (Figure 1) while the molecular weight, $\bar{M}_n$, decreases linearly by over 2 orders of magnitude with increasing concentration of cobalt catalyst (Figure 2). As expected for a typical polymerization, the rate of polymerization increases linearly with the square root of the concentration of the azo initiator and no polymerization occurs in the absence of the initiator.

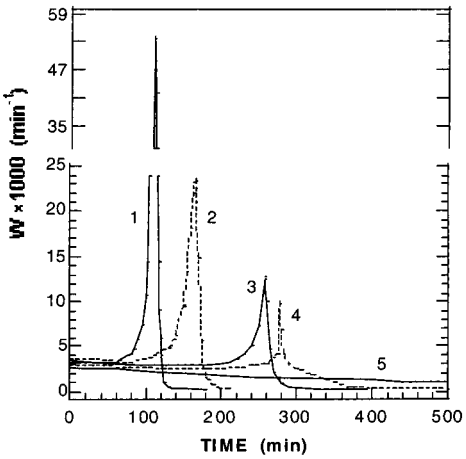


Figure 1. Temporal dependence of the rate of polymerization of bulk MMA under CCT conditions.

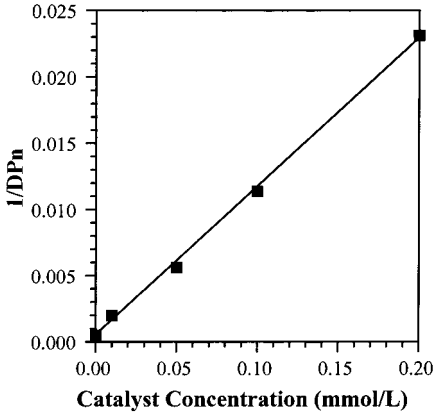


Figure 2. Dependence of $(DP_n)^{-1}$ on the concentration of Co^{II}mesoporphyrin-II.

Free-radical polymerizations of bulk monomers are subject to the gel effect or Trommsdorff effect.[16] Figure 1 also indicates that CCT suppresses the gel effect. Because the resulting product is lower in molecular weight, the viscosity of the polymerizing medium is not as high at a given degree of conversion. Thus, the observed sharp maxima in the rates of polymerization at time τ can be used as a quantitative measure of the chain-transfer constant of CCT.[17] At 60 °C in a bulk polymerization of MMA initiated with 0.04 mol/L AIBN, the following empirical equation relates the chain-transfer constant of CCT, k_C, to the concentration of cobalt catalyst, LCo, in mol/L and the time of maximum polymerization rate, τ, in minutes[18]

$$\frac{400}{\tau} = 3.6 - \lg(k_C[LCo]) \qquad (1)$$

The linearity of this relationship is demonstrated in Figure 3. Any deviation from linearity from eq 1 indicates complications in the course of the polymerization. The complications are typically catalyst poisoning or polymerization retardation (see section 3.6).

The cobalt porphyrin, PorCo, was recovered from the product by flash chromatography and reused several times without any detectable change in molecular structure, clearly indicating the catalytic

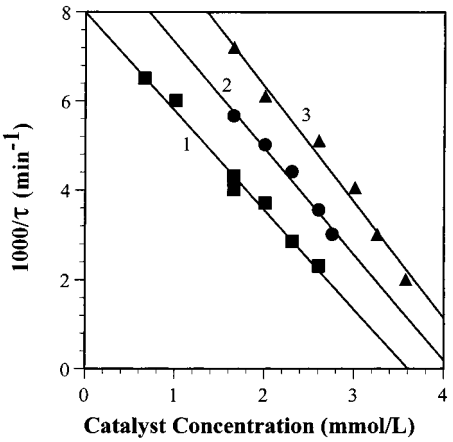
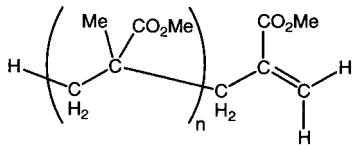


Figure 3. Dependence of reciprocal time of the maximum polymerization rate on the concentration of catalyst for Co^{II}-mesoporphyrin-II (1), Co^{III}(pyridine)bis(dimethylglyoximato) iodide (2), and Co^{II}tetra-*tert*-butylbenzoporphyrin (3).

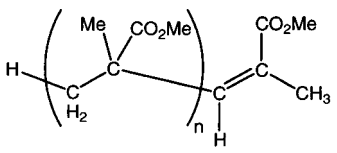
character of the process of molecular weight reduction.

NMR analysis of the resulting oligomers,[19−22] supported by IR spectroscopy[23] and labeling experiments,[19] indicated that the product of methyl methacrylate polymerizations is **3**.



3

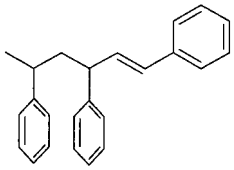
The same species has been observed in the spontaneous polymerization of MMA, but its yield is limited to at most 50% because it arises from disproportionation of two radical chains.[24] In low productivity polymerizations, some product derived from the initiating radical could be observed, but in high conversion polymerizations, it appeared that virtually all of the product molecules were initiated with a hydrogen atom and terminated with an olefinic end group. This polymeric product can be formed in the presence of cobalt porphyrin only by hydrogen transfer from the α-methyl group of methacrylate end unit of the propagating radical to monomer. The turn-over number of this reaction was calculated to be at least 10^6, while selectivity is virtually quantitative.[2,25,26] It is the quantitative nature of the double bond formation that makes this new product useful in a number of applications. It is interesting that the isomeric compound, **4**, is not observed in the reaction mixture even though it is more stable thermodynamically.[27]



4

The kinetic preference for **3** could be attributed to steric screening of the internal methylene protons near the tertiary carbon center through their interaction with the large planar porphyrin molecule.

Styrene lacks a methyl group on the propagating radical, so chain termination must lead to a different type of product. A thorough analysis has led to the conclusion that the product is terminated exclusively by a trans substituted olefinic group.[28] For example, the trimer is **5**.



5

One of the most striking features of CCT is the exceptionally fast rate at which it takes place. The molecular weight of a polymer can be reduced from tens of thousands to several hundred utilizing concentrations of cobalt catalyst as low as 100−300 ppm or $\sim 10^{-3}$ mol/L. The efficiency of catalysis can be measured as the ratio between the chain-transfer coefficients of the catalyzed reaction versus the noncatalyzed reaction. The chain-transfer constant to monomer, C_M, in MMA polymerization is believed to be approximately 2×10^{-5}.[29] The chain-transfer constant to catalyst, C_C, is as high as 10^3 for porphyrins and 10^4 for cobaloximes. Hence, improved efficiency of the catalyzed relative to the uncatalyzed reaction, C_C/C_M, is $10^4/10^{-5}$ or 10^9. This value for the catalyst efficiency is comparable to many enzymatically catalyzed reactions whose efficiencies are in the range of 10^9-10^{11}.[18] The rate of hydrogen atom transfer for cobaloximes, the most active class of CCT catalysts to date, is so high that it is considered to be controlled by diffusion.[5,30−32] Indeed, k_C in this case is comparable to the termination rate constant.[33]

The very high rates of catalytic chain transfer finally made it practical to prepare low molecular weight oligomers by free-radical polymerization. The chemistry of low molecular weight oligomers was relatively unexplored for several reasons. Previous routes to oligomers involved complicated and unpleasant chemistry or were very expensive. Thiol chain termination required high levels of chain-transfer agents, leaving high levels of toxic or malodorous residues. It is also possible to obtain low molecular weight species by utilizing high levels of initiator, but in addition to being expensive, high levels of azo initiators can lead to toxic cross-coupling products. Living polymerizations required high levels of initiator or catalysts because each initiator leads to only one macromonomer, making them commercially unattractive when low molecular weights are required. A further reason was that the main objective of polymer science had generally been the synthesis of high molecular and even ultrahigh molecular weight species, primarily to improve mechanical properties. Recent changes in industrial requirements have brought lower molecular weight species into focus. For example, the lower solvent content required to meet low VOC constraints for paints[34] brings renewed interest in low-viscosity oligomers that can be cured during or shortly after application.[35,36] Highly structured pigment dispersants for paints and other applications are often based upon block copolymers[37] accessible through macromonomers, and ink-jet printers require sophisticated polymer formulations to achieve the very rigorous set of demands placed upon those systems.[38]

The Mayo equation is often used to determine chain-transfer constants.[39] C_s is determined from measurements of DP_n over a range of [S]/[M] with the provison that DP_n^0 remains constant throughout the range evaluated.[40,41] A plot of $1/DP_n$ versus [S]/[M] yields a straight line with a slope of C_s and intercept of DP_n^0. Catalytic chain transfer obeys the Mayo equation well for DP_n of 20 and higher. When DP_n is less than 20, there is an apparent deviation from linearity for DP_n versus the concentration of the cobalt catalyst. This phenomenon was observed for methacrylate.[14] It appears that at low molecular weights or high catalyst concentrations, the catalyst is loosing activity (Figure 4).

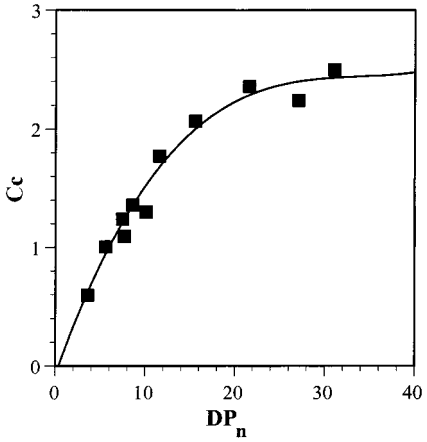


Figure 4. Dependence of the average chain-transfer constant on the number-average degree of polymerization. Data are taken from ref 14.

This unusual behavior was detected for measurements of polydispersity as well. While polydispersity is close to 2 for $DP_n > 20$ as expected for free-radical polymerizations in which there is a high level of chain transfer,[40,42] the polydispersity index decreases to values approaching 1.1−1.2 for $DP_n < 10$. To explain this unusual behavior for C_C, low MMA oligomers were separated into fractions by HPLC[43] and C_C was calculated for each individual radical, $C_{C(n)}$. The resulting dependence of $C_{C(n)}$ on DP is shown in Figure 5.

$C_{C(n)}$ stays unchanged for DP values down to 6, and then it starts to diminish rapidly. C_C by definition is an "average" term, and as a result, it does not change as rapidly with decreasing degree of polymerization as does $C_{C(n)}$. Having determined $C_{C(n)}$ for each "n", one can now plot the calculated dependence of C_C against DP_n. The calculated dependence does not correlate well with the earlier results.[14] In fact, evidence that indicates that C_C decreases with increasing chain length has been reported.[44,45] A viable

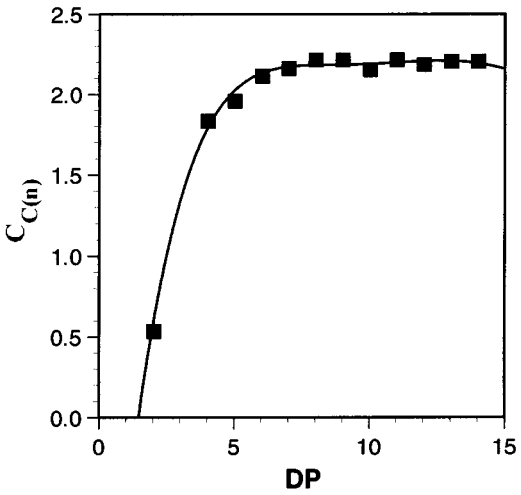


Figure 5. Dependence of $C_{C(n)}$ on DP.

explanation for the ambiguity at these low molecular weights was not recognized until later.[46,47]

As mentioned above, free-radical oligomerizations of acrylates to DP of less than 10 were little explored at the time that CCT was discovered. Methods of polymer characterization developed for high molecular weight polymers begin to fail at these low oligomers, though new methods are being developed.[48,49] End groups are generally not important in the chromatography of high polymers. With the decrease of molecular weights down to several hundred, the physical effects of end groups become more important. They can change fundamental parameters such as refractive indexes and UV absorptions. Because UV absorption and refractive index, primary tools for detection in chromatographic techniques, were dependent on DP_n, quantification of analyses was made more difficult.[46,47] Figure 6 shows that

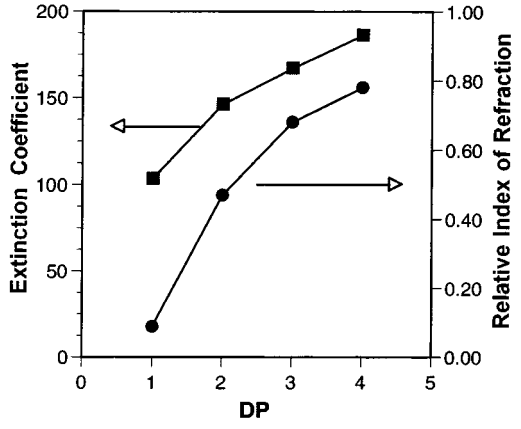


Figure 6. Dependence of the extinction coefficient and relative index of refraction of low MMA oligomers on the degree of polymerization.

these parameters for MMA dimers differ from those of high polymer by over 50% with smaller differences for higher oligomers. For example, if a solvent with a refractive index close to that of MMA dimer is used in the analysis, errors can be substantial. In an extreme example, the use of toluene for the analysis would give inverse peaks for all of the low oligomers while high polymer would give a positive peak. Some moderate oligomers would be invisible to the analysis. Failure to consider the change in physical properties of low oligomers may result in substantial differences between the calculated and observed dependence of C_C on DP_n. Molecular weights for higher polymers may be transformed via the known Mark−Houwink−Sakurada (MHS) constants for poly(methyl acrylate).[50] The MHS constants should be used only for a specified molecular weight range because at low molecular weights the MHS constants are a function of chain length.[51] A similar effect has been quantified in styrene oligomers, and the effect is detectable out to hexamers.[28]

The terminal double bond becomes an issue in the thermodynamic calculation of conversion as well. Polymerization of olefinic molecules can generally be described as the conversion of double bonds into two single bonds. While not an issue for high polymers, any double bonds remaining in the final product decrease the thermodynamic parameters associated with this process. Thus, the heat of polymerization in the CCT process decreases according to eq 2[52]

$$\frac{\Delta H_n}{\Delta H_\infty} = \frac{\mathrm{DP_n} - 1}{\mathrm{DP_n}} \tag{2}$$

where ΔH_n is the heat of polymerization when the degree of polymerization equals n and ΔH_∞ is the heat of polymerization for high polymer. For $DP_n > 8$, the resulting error would be less than 10%, but with MW reduction below this number, the effect of the chain end becomes more pronounced. Other parameters, like the volume reduction during polymerization, should follow the same pattern. The reduction in the heat of polymerization could be one of the reasons for the reported[12] minor (<20%) reduction of initial catalyst activity when concentrations of active catalysts are greater than 0.005 mol/L. Another reason for reduction of catalyst activity at the beginning of polymerization is the formation of $LCo-R_n$ (section 3.2).

A full understanding of polymerizations resulting in $DP_n < 8$ requires additional theoretical consideration and reevaluation of many of the well-known and widely used equations and relationships. The Mayo equation (eq 3) provides a good example of a relationship established for high polymer that fails when extended to oligomers.

$$\frac{1}{\mathrm{DP_n}} = \frac{1}{\mathrm{DP}_{n0}} + \frac{k_C[\mathrm{LCo}]}{k_P[\mathrm{M}]} \tag{3}$$

M is monomer, and DP_n and DP_{n0} are the number-average degree of polymerization corresponding to those obtained with and without chain-transfer agent. In an extreme, at elevated levels of an active catalyst (for example $k_C = 10^7$ L/mol·s and [LCo] = 0.01 mol), the calculated DP_n can be less than 1, clearly an impossible situation. Hence, the Mayo equation in its standard form is not applicable for many cases of CCT when low oligomers are being prepared. Redetermination of the dependence of the number-average degree of polymerization on the concentrations of

monomer and CCT catalyst concentration in the short-chain approximation gives eq 4[52]

$$\frac{1}{DP_n - 2} = \frac{1}{DP_{n0}} + \frac{k_C[LCo]}{k_P[M]} \quad (4)$$

For high polymer, eq 4 is indistinguishable from eq 3. For the case of intensive CCT, when the MW of the resulting product is low, eq 4 can be reduced to eq 5

$$DP_n = 2 + \frac{k_P[M]}{k_C[LCo]} \quad (5)$$

There also arises an interesting semantic issue. Equation 5 indicates that product lower than the dimer cannot be obtained by CCT. Clearly, the actual degree of polymerization is quantized in units of one and DP_1 is called "starting material". Nonetheless, at high levels of an active catalyst, starting monomer is frequently converted to radical and then back to "monomeric product" before addition of a second monomer can occur. At $DP_n < 12-15$, deviation from the linear dependence of DP_n on the concentration of catalytic chain-transfer agent are observed as expected.[14] At the same time, the polydispersity (if this is a meaningful term) narrows and becomes dependent upon DP_n according to eq 6

$$\frac{DP_w}{DP_n} = 2 - \frac{3}{DP_n} + \frac{2}{(DP_n)^2} \quad (6)$$

This expression also differs from the text book definition. Hence, the observed narrowing of polydispersity and reduction of observed catalytic activity in CCT under high concentrations of an active catalyst has, at least in part, kinetic origins.

To understand the distribution of products in the low-MW region, it is important to realize that for low molecular weight polymeric radicals, the many different chain-transfer constants may depend on DP_n. The length dependence of chain-transfer constants for short radicals can be significant. Thus, k_P of the dimeric radicals of MMA and MAN are about 20 times higher than those of high polymeric radicals, but the difference diminishes rapidly with growth of the radical. Pulsed-laser methods have been utilized extensively for the determination of free-radical polymerization kinetics and have been the subject of a review.[50] The technique allows the investigation of chain length dependence not only for chain propagation but also for chain termination.[53−56] Care must be taken in doing the experiments and utilizing the results.[57] Other techniques involving nitroxides[58] and computational chemistry[59] have been suggested. Nonetheless, the pulsed laser technique remains the IUPAC-recommended approach.[60]

The difference in propagation rate constants of the low molecular weight species was also demonstrated using a technique based upon CCT. At high rates of CCT, only small radicals are present in the system. This makes it possible to measure the rates of propagation and chain transfer separately by gradual changes in the concentration of chain-transfer catalyst.[61] Discussion of the absolute propagation rate constants of small radicals is not related directly to the purpose of this review, but there are two points worth making.

First, the chain-transfer coefficient, k_C, is almost independent of radical lengths despite the array of claims in the literature.[44−47] Thus, k_C of the meso-tetraphenyl derivative of Co−porphyrin with the dimeric MMA radical is 2.8×10^6 L/mol·s versus 2.4×10^6 L/mol·s for high polymer. As a result, C_C decreases with DP_n because $C_C = k_C/k_P$. The reason that k_C is independent of the size of the radical is not clear. CCT seems to be diffusion controlled, and the large size and required orientation of the porphyrin molecule may be controlling. It cannot be excluded that the rate of CCT is determined by the rate of formation of intermediate species such as a caged radical pair. In the latter case with low molecular weight species, one might observe length dependence of the k_C for highly active CCT catalyst, like cobaloximes.

The second significant point is that propagation in the presence of the cobalt catalyst occurs by a free-radical mechanism, not by a coordination polymerization mechanism described by eqs 7−9 as suggested in some publications.[2,62−64]

$$LCo - R_n + M \rightarrow LCo - R_{n+1} \quad (7)$$

$$LCo - R_n \rightarrow LCoH + P_n^{=} \quad (8)$$

$$LCoH + M \rightarrow LCo - R_1 \quad (9)$$

The main evidence is that the values of k_C for the small radicals obtained with the CCT-based method are very close to those obtained by other methods.[55,65] This is not to say that formation of a Co−C bond does not occur; it is simply not an important step on the catalytic cycle.[66] It does, however, remove catalyst from the catalytic cycle.

To conclude the introduction, all of the phenomena of CCT are fully explained by normal free-radical polymerization once a short-chain approximation has been applied. Experimental data indicates that the short-chain approximation becomes important for $DP_n < 15$ and $DP < 6$. Equations 4−6 were obtained with the simplifying assumptions that chain-transfer constants do not depend on the degree of polymerization, though this is known to be incorrect. Nonetheless, they provide a closer description of reality than do the descriptions formulated for high polymer. The exact dependence of DP_n and DP_w requires knowledge of all rate constants for each radical.

Theoretical investigations have been used to model coenzyme B_{12}. While important conclusions may be drawn, the work has not been extended with CCT in mind. Due to computational limitations, the initial work was limited to the triaminomethylcobalt^{III}−amide system.[67] Force fields specifically designed to do molecular mechanical calculations on cobalamins[68] and cobaloximes[69] are relevant for conformational studies but cannot elucidate the mechanisms of cobaloxime reactions because they do not account for electronic effects. Computational investigation of

Table 1. Effect of Substituents on MMA CCT Activity for Cobaloximes 6[a], 7[b] and 8

compound	X_1	X_2	A or E	E (base)	C_C	ref
6a	Me	Me	Me	H_2O	<50	77
6b	$-(CH_2)_4-$		Et	H_2O	<50	77
6c	Me	Me	CN	Py	<50	77
6d	Me	Me	NO_2	Py	<50	77
6e	Ph	Ph	CN	Py	<50	77
6f	Ph	Ph	Et	H_2O	<50	77
6g	Me	Me	Cl	Py	5 000	77
6h	Me	Me	I	Py	1 000	77
6i	Me	Me	CNS	Py	4 000	77
6j	Me	Me	sec-Bu	H_2O	13 000	77
6k	Ph	Ph	CNS	Py	25 000	77
6*l*	Me	COOEt	Cl	Py	12 000	77
6m	Me	COMe	Cl	Py	25 000	77
6n	$-(CH_2)_4-$		Cl	Py	4 000	77
6o	α-furyl	α-furyl	Cl	Py	100 000	77
6p	Ph	Ph	Cl	H_2O	25 000	77
6q	Ph	Ph	Cl	Py	30 000	77
6r	Ph	Ph	Cl	$P(Ph)_3$	100 000	77
6s	Me	Me	Py	Py	2 100	78
6s[e]	Me	Me	Py	Py	700	79
6t	Me	Me	NEt_3	NEt_3	1 600	78
6u	Me	Me	PPh_3	PPh_3	4 100	78
6u	Me	Me	PPh_3	PPh_3	20 000	44
7a			Cl		11 000	77
7b			ClO_4		<50	77
7c			NO_3		<50	77
8a[c]	Me	Me			11 000	77
8b[d]	Ph	Ph			66 000	77

[a] Run in bulk MMA at 60 °C. [b] Measured in MMA:methanol = 7:3 v/v at 60 °C. [c] MMA:methanol = 7:3 v/v. [d] MMA:methanol = 7:3 v/v + 1% Py. [e] MMA:methanol = 1:1 v/v.

relative bond-breaking energetics requires quantum mechanics, and until recently, few calculations have been attempted because of their large size. Semiempirical models have been important in the discussion of the balance between steric and electronic effects in B_{12} reactions,[70] but they are not effective for the determination of equilibrium structures. DFT calculations are expected to provide higher accuracy. Calculation of nuclear quadrapole couplings of simple coenzyme B_{12} models without a planar framework proved to be reasonable.[71] The B3LYP method has been used to evaluate the equilibrium structures of corrin models with different axial alkyl groups.[72] The equilibrium structures of methyl B_{12} and adenosyl B_{12} have a different electronic structure for the two Co−C bonds. The HOMO energy is higher in $AdoB_{12}$ than in MeB_{12}, favoring homolytic cleavage because of the 5′-deoxyadenosyl group that induces more electron density on cobalt. This may explain part of the homolysis heterolysis dichotomy. Comparison of the computational geometries with experimental results[73] suggests two very different reaction coordinates for the two coenzymes related to competitive heterolysis or homolysis of the two respective Co−C bonds.[74] Unfortunately, these studies invoke chemical and structural differences that are not available to the catalysts in CCT.

2. Catalysts

2.1. Catalyst Screening

Testing new compounds for catalytic chain-transfer activity in free-radical polymerizations is an interesting science and art. Choosing the optimal testing conditions is crucial for getting reliable results. Side reactions can both mask and mimic CCT so that considerable judgment is required. The results of polymerization in the presence of cobalt chelates depend on temperature, solvent, pH, the sterics and electronics of the chelating ligand, the presence of additional ligands, and the monomer chosen. Minute concentrations of impurities, particularly oxygen,[75,76] in the reaction media or even in the tested complex may corrupt the results. The issue of polymerization conditions will be discussed later in section 3.7 and to a lesser extent in other sections. Redox or other reactions in the polymerization media, changes in the rate constants due to presence of solvents, and other phenomena can lead to reduction of MW in the absence of CCT. One generally expects a profound effect, so when $C_C < 50$, the presence of CCT can be questionable. This is not to say that cobalt chelates with $C_C < 50$ are not CCT catalysts, but confirmation requires additional investigation.

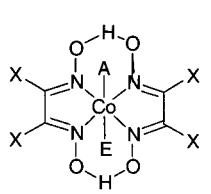
Table 2. Influence of Cobaloximes 6 Substituents on CCT Activity in Styrene[a] [77]

compound	X_1	X_2	A	E (base)	C_C
6a	Me	Me	Me	H_2O	<4
6d	Me	Me	NO_2	Py	<4
6e	Ph	Ph	CN	Py	<4
6g	Me	Me	Cl	Py	450
6n	$-(CH_2)_4-$		Cl	Py	300
6q	Ph	Ph	Cl	Py	350
6r	Ph	Ph	Cl	$P(Ph)_3$	500

[a] Bulk styrene, 60 °C.

Unless otherwise mentioned in the text, all scouting for CCT reported here was carried out at 60 °C in MMA or in a methanol solution of MMA if LCo was not directly soluble in monomer. AIBN was used as the azo initiator because peroxides often decompose or poison the cobalt complexes.

The best known CCT catalysts are cobaloximes having the general structures **6**, **7**, **8**, and **9**.[77−81] Data on their catalytic activities in MMA and styrene polymerizations are presented in Tables 1 and 2, respectively.



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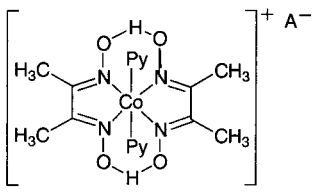

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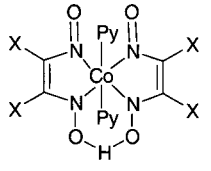

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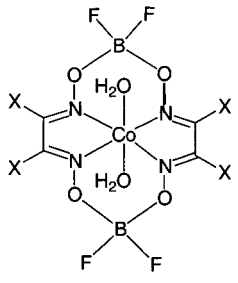


9

As a result of the ready availability of required starting material and smooth, well-developed syntheses,[82] the cobaloximes **6**−**8** served as convenient models for understanding how axial ligands and substituents on the macrocyclic ligand affected the catalytic behavior of these Co^{II} species.[83] There are some advantages to using the Co^{III}−alkyl versions of these catalysts.[84] The macrocyclic ligand in cobaloximes is an almost perfectly planar structure carrying a formal double negative charge. The hydrogen bonding between the two monoanionic covalent halves of the equatorial ligand is sufficient to confer considerable structural rigidity and chemical stability.[85−88] The complexes are able to withstand strong acids[89,90] and even Grignard reagents.[91] In deuterium oxide solutions, replacement of the bridging hydrogen atom with deuterium is slow even in the presence of bases or acids.[92,93] This stability allows the catalysts to be employed in aqueous systems as well as organic media.[94]

The axial ligands can be divided into two groups. Group A comprises monoanionic ligands that result in an oxidation state of three in cobalt. These may be the anions resulting from acido ligand (for instance chloride) or may be alkyls. The hydride ligand would also fall into this category and plays an important role in the catalytic chemistry, but in general, they have not been observed directly. Electron-donating ligands, E, are neutral, Lewis base ligands which are coordinatively bound and are not involved in the oxidation state of the cobalt. From a practical point of view, E ligands, particularly water, are often present in the catalysts employed for CCT, but they are often unspecified.

2.2. Cobalt Catalyst Activities

As shown in the Table 1, the activities of cobaloximes **6** can vary by more than 3 orders of magnitude.[77−81,95,96] Ligands of class A showed no catalytic activity when A = primarily alkyl, CN, or NO_2 (entries **6a** through **6f**). When A is halogen, pseudohalogen, or secondary alkyl (entries **6g**−**6k**), the resulting cobaloximes are potent chain-transfer catalysts. Variation of substituents on the dioximate moieties (entries **6L**−**6o**) changes the CCT chain-transfer constants severalfold. The presence of ligands of the E type (entries **6p**−**6r**) also cause variations of severalfold, and it seems at first glance that C_C increases with the strength of their ligand field.

For charged cobaloximes such as **7**, the choice of the A ligand is crucial (Table 1). Differences in this catalytic activities of these cobaloximes with chloride and other acido ligands range over 3 orders of magnitude. $Cobalt^{III}$ oximes **8** with no A ligands are among the most active. These observations are consistent for both MMA and styrene as monomer (Table 2).

Cobaloximes with structure **9** have a BF_2 bridge rather than the more usual hydrogen atom bridge between the two dioxime moieties. Such a modification leads to better stability of the $cobalt^{II}$ oximes toward oxidation by oxygen by air. While of little consequence in an academic laboratory, it is important on a commercial scale that the compounds can be stored and handled by chemical operators without special precautions.[97−100]

It is difficult to compare the activities of the H-bridged $cobalt^{II}$ oximes with their BF_2-bridged counterparts because of their increased sensitivity to oxygen. The in situ preparation of $cobalt^{II}$ oximes in radical polymerization of MMA has been described.[79] Making such cobaloximes in situ requires methanol, pyridine, or other solvents to dissolve the starting materials, and as a result, the concentrations of the monomers are 70% or less in the final solution. In one example, the data indicate $C_C \approx 700$ for Py-$(dmgH)_2Co^{II}$,[79] which is substantially less than that of the $cobalt^{III}$ oximes shown in Table 1. A second approach for in situ synthesis is to use starting materials such as cobalt 2-ethylhexanoate that are soluble in MMA, thereby making additional solvent unnecessary.[101]

Traditional methods of handling air-sensitive materials[102] are generally appropriate for making $cobalt^{II}$ dioximes because cobaloximes of the type $E(dmgH)_2Co^{II}$ tend to dimerize and precipitate from methanol solutions. Thus, $(PPh_3)(dmgH)_2Co^{II}-Co^{II}(dmgH)_2(PPh_3)$ was synthesized and tested in bulk MMA to give a relatively unusual result. The catalytic activity of such LCo depends on the concentration and ranges from $C_C = 800$ to $C_C = 20\,000$.[44] The reasons for such a distribution of C_C values will be detailed later. At this point it is sufficient to indicate that the catalytic activities of cobaloximes **6**−**8** depend very much on axial ligands of the A type and much less on substituents in the equatorial ligand and ligand of the E type. The latter two may change the chain-transfer constant 2- to 4-fold, while ligands of the A type may reduce C_C by orders of magnitude. The A ligands giving the highest activities are halides, especially chloride. E type ligands tend to increase C_C with increasing ligand strength as one may see in Table 1 (phosphines > py > H_2O).[78] The same results were observed in porphyrins, although the effect is smaller than in cobaloximes perhaps due to a larger "electron pool".

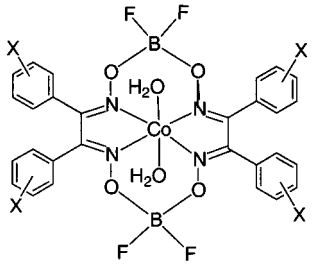
When cobaloximes, **9**, with a BF_2-bridging ligand,[103,104] were first reported as CCT catalysts,[105,106] they quickly became the CCT catalysts of choice.[44,107−117] They are often introduced into the reaction mixture as either Co^{II} or Co^{III}−alkyl species. It is presumed that the Co^{III}−alkyl species are quickly and quantitatively reduced to Co^{II} in situ.[77,118] Data on their activity are reported in Table 3. Substituents in the cobaloximes **9** have a slight effect on the catalytic activity but more surprising is the dependence of C_C on solvents employed for the polymerizations (see Tables 2 and 3). In one case the dependence of C_C on solvent was traced to impurities, presumably acids, in butanone.[115] Freshly distilled butanone does not reduce the CCT chain-transfer constant. In another case C_C was found to be dependent upon impurities in the initiator.[76] Regardless of the origin of the solvent effect, the existence of such an effect makes it difficult to extrapolate observations

Table 3. Catalytic Activity of Cobaloximes, 9,[a] in MMA CCT[105,112,115−120]

			C_C				
entry	X	X	THF	butanone	methanol	toluene	bulk
9a	Me	Me		27 000	11 000−20000		41 000
9b	2-C_4H_3O			7 200			
9c	C_6H_5	C_6H_5		20 500		23 000	18 000−20 000
9d		$-(CH_2)_4-$					14 000
9e	4-MeC_6H_4	4-MeC_6H_4	25 000				
9f	4-EtC_6H_4	4-EtC_6H_4	27 000				
9g	4-^{i}PrC_6H_4	4-^{i}PrC_6H_4	25 000				
9h	4-tBuC_6H_4	4-tBuC_6H_4	21 000				
9i	4-BrC_6H_4	4-BrC_6H_4	15 000	4 500			
9j	4-$MeOC_6H_4$	4-$MeOC_6H_4$	15 000	7 000			
9k	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	5 000	5 000			
9L	4-BrC_6H_4	4-$SO_3NaC_6H_4$			7 300		
9m	3-MeC_6H_4	3-MeC_6H_4	28 000				
9n	2-MeC_6H_4	2-MeC_6H_4	16 000				

[a] Monomer is MMA, 60 °C.

made in solution polymerizations in the presence of **9** or the subset of complexes



to emulsion or suspension polymerizations reported in Table 3.[119]

In cobaloximes **6**−**8** it could be concluded that electron-withdrawing groups (EWG) increase C_C. Compare, for example, entries **6g**, **6L**−**o**, **8a**, and **8b** in Table 1. Table 3 does not afford the same conclusion.

For cobaloxime **9a**, chain-transfer constants obtained using the new CLD techniques of rate constant calculations[40,122] were $C_C = 25\,000$ for MMA and $C_C = 660$ for styrene polymerization at 60 °C.[123,124] In other cobaloximes, a reverse trend was observed, with electron-donating substituents (entries **9e**−**h** in Table 3) increasing activity while EWG (entries **9i**−**L** in Table 3) led to a decrease relative to hydrogen (**9c**, Table 3). The data of Table 3 can be explained by the presence of the strong EWG, BF_2, in cobaloximes **9**.[97] The electron-withdrawing group reduces electron density on cobalt to the extent that the lone electron on Co^{II} behaves less like a free radical. Electron-donating substituents in the equatorial ligands of **9** help to restore the free-radical properties of the cobalt atom, while additional EWG in the equatorial ligand exacerbate the electron density problem on cobalt. This explanation leads to the conclusion that some value of electron density on the cobalt atom is required for optimal hydrogen atom abstraction during CCT.

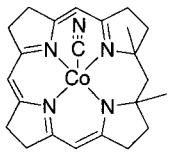
The effect of solvents on the properties of BF_2-bridged cobaloximes in methacrylate CCT carries over to polymerization of styrene. Thus, for cobaloximes **9** in the polymerization of styrene, $C_C = 500$ in butanone[120] while $C_C = 1400$ in bulk.[115] Cobaloxime **9c** showed $C_C = 700$ in bulk styrene polymerization,[115] a value 20−30 less than C_C in polymerization of methacrylates. This is similar to that observed for cobaloximes, **6** (Table 1), and for cobalt porphyrins, although in the last case the kinetic picture is more complex. Interestingly, the rate of CCT in styrene polymerization has been shown to be light dependent.[125] The rate was found to be less that 100 in the dark but increases to a maximum value of $C_C = 5000$ under UV irradiation. The value of C_C was also found to be dependent upon the initiator concentration, decreasing with higher initiator levels. Apparently, UV irradiation homolyzes the $Co^{III}-C$ bond formed by addition of styrene radical to the Co^{II}.

Viscosity of the medium can also play a role in the kinetics due to the importance of diffusion in the observed rate constants. In the bulk radical polymerization of 2-phenoxyethyl methacrylate, thiol chain-transfer reagents operate at rates close to those observed for MMA while the rate of CCT catalyzed by **9a** is an order of magnitude slower (2×10^3 at 60 °C) than that of MMA.[5] The thiol reactions involve a chemically controlled hydrogen transfer event, whereas the reaction of methacrylate radicals with cobalt are diffusion controlled. The higher bulk viscosity of the 2-phenoxyethyl methacrylate has a significant influence on the transfer rate.

The chain-transfer reaction is essentially unchanged in going from bulk polymerization to toluene solution.[30] In the low-viscosity medium, supercritical CO_2, chain transfer was found to be significantly enhanced by an order of magnitude (10^8 L mol^{-1} s^{-1}) compared with toluene or bulk MMA as a medium. Again, the results are consistent with a diffusion-controlled rate-determining step.[30] However, another report indicates no enhancement of chain transfer in supercritical CO_2.[126] This discrepancy may be the result of the necessity of using different catalysts in the two media.

While on the subject of polymerization media, there is also a report of CCT in ionic liquids.[127] 1-Butyl-3-methylimidazolium hexafluorophosphate is a room-temperature ionic liquid. Although such liquids have been found to be excellent solvents for a number of chemical transformations, there are few reports of polymerizations.[128] Nonetheless, Co^{II}-mediated cata-

Table 4. Values of C_C in MMA Polymerizations for a Variety of Cobalt Complexes[a]



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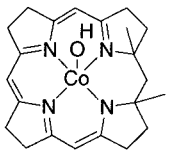

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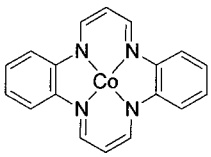

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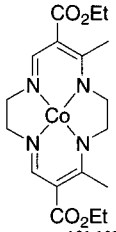

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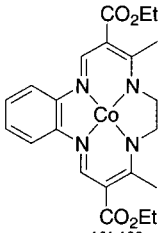

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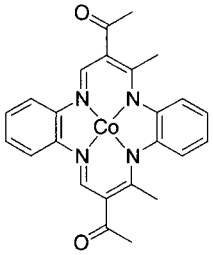

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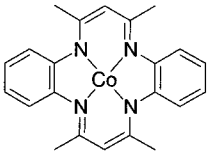

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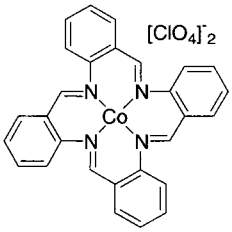

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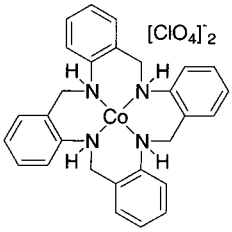

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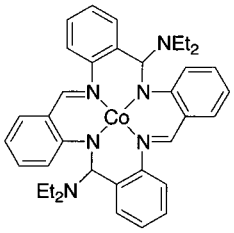

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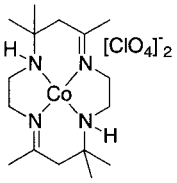

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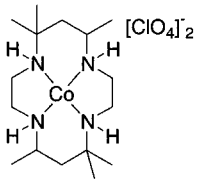

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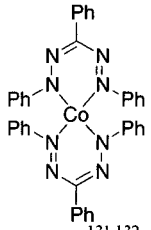

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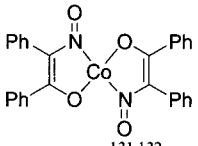

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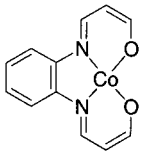

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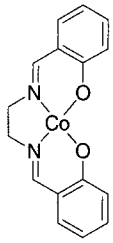

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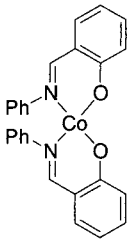

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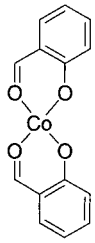

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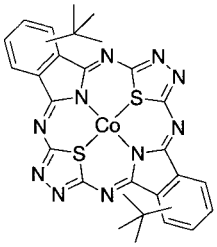

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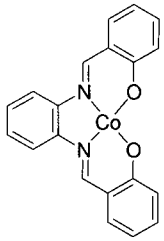

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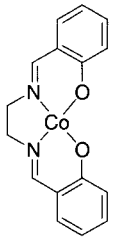

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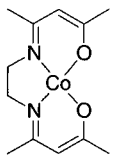

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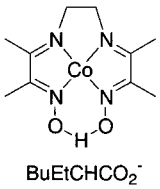
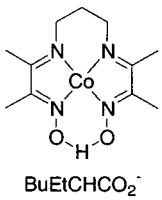


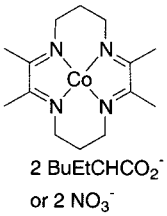
BuEtCHCO$_2^-$

32, 600[101]



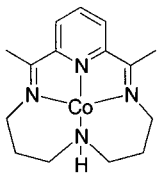
BuEtCHCO$_2^-$

33, 500[101]



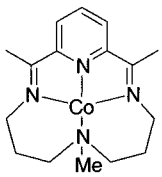
2 BuEtCHCO$_2^-$
or 2 NO$_3^-$

34, 170[101, 134]



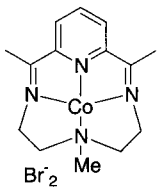
X$^-_2$

35[133]
Br, 650
OAc, 670
CNS, 900



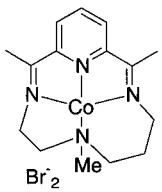
Br$^-_2$

36, 130[133]



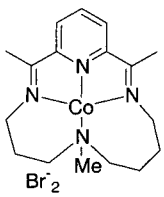
Br$^-_2$

37, <10[133]



Br$^-_2$

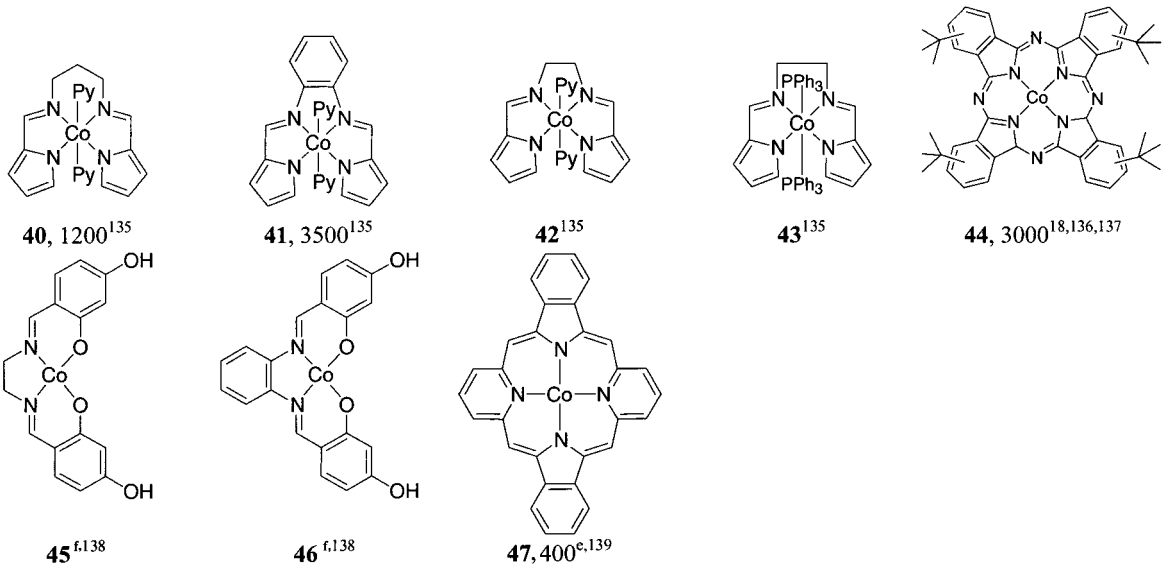
38, <120[133]



Br$^-_2$

39, 120[133]

Table 4. (Continued)



40, 1200[135] **41**, 3500[135] **42**[135] **43**[135] **44**, 3000[18,136,137]

45[f,138] **46**[f,138] **47**, 400[e,139]

[a] In many instances, there were unspecified axial ligands present. [B] Cobalamin substituents not shown. [c] Catalytic inhibition in L/mol·sec. [d] Irradiated with sunlamp. Temperature is unknown. [e] In MMA/DMF = 9:1 at 60 °C. [f] LRP initiators.

lytic chain transfer has been observed in the radical polymerization of MMA.

Polymerization of MMA both thermally and photochemically in the ordered media, cholesteryl oleyl carbonate and cholesteryl 2-ethylhexyl carbonate, were studied in the presence and absence of cobalt tetraphenylporphyrin. The percentage conversion and molecular weight were lowered in the presence of CoTPP for thermal polymerizations. In photopolymerizations, the percentage conversion was high and the molecular weights were low.[129]

In the photodecomposition of polystyrene-bound cobaloximes, the polymer chain decreases the mobility of bis(dimethylglyoximato)pyridinecobalt(L) and increases the probability of recombination of L and a radical fixed on the polymer chain. Retardation of the dissociation resulted in a larger equilibrium constant for the polymeric system than that for the analogous monomeric system.[130]

Table 4 presents C_C for a variety of catalysts other than cobaloximes that have been tested in MMA radical polymerizations.[101,109,131−136] In addition, the following values have been reported: MMA, C_C = from 3×10^5 to 2.4×10^5 (from 40 to 70 °C, **9a**);[31] and $C_C = 1.9 \times 10^4$, $k_{Co} = 1.6 \times 10^6$ M^{-1} s^{-1} (60 °C, **9c**).[5] Where data at several temperatures are available, C_C is relatively independent of temperature because k_P and k_{Co} change at approximately the same rate.

It is clear that cobalt catalysts **10**−**44** are much less active than cobaloximes, generally by 2 orders of magnitude. It is concluded that the hydrogen transfer reaction is not diffusion controlled in their case. This difference in reactivity also suggests that some of the trends found for cobaloximes may not work for other cobalt chelates. Unfortunately, there have been few studies to this end. Most of the values of C_C in Table 4 were calculated having only one or two points on the Mayo dependence. For cases when $C_C < 50$, it is usually necessary to carry out additional experiments to confirm that the reduction in molecular weight is actually due to CCT rather than other reactions including noncatalytic chain transfer. As a reasonable indication of the accuracy of the chain-transfer constant measurements, the C_C of compound **30** (salcomine) was found to range from <50 to 150.

It is clear that a core of four nitrogen atoms in the coordination center is crucial for active CCT. Replacement of two nitrogen atoms with oxygen (**23**−**26, 29**−**31**) or sulfur (**28**) essentially shuts down the ability of LCo to abstract hydrogen from free radicals. Compound **28** is particularly interesting because of the similarity of molecular structure of this chelate to cobalt phthalocyanines, which are known to be good CCT catalysts.

The influence of axial ligands on cobalt dimethylglyoxime complexes holds for these other ligands. Axial ligands that preclude CCT by cobaloximes (e.g., CN) also interfere with the ability of cobalamin **10** to react with radicals. When hydroxyl is the A ligand on cobalamin (**11**), it does not interfere with hydrogen transfer. Halogen, pseudohalogen, and carboxylic acids are "good" ligands. Somewhat surprisingly, in **34**, NO_3^- is also "good" for CCT while in cobaloximes such ligands resulted in the absence of catalytic activity.

The presence of four nitrogen atoms coordinated in the equatorial plane in LCo does not guarantee noticeable catalytic properties. It would be of interest to determine the factors that control activity. One explanation suggests that only low-spin LCo can be CCT catalysts.[109] Thorough investigation indicated, however, that this could be a necessary but is not a sufficient condition. For example, CCT catalysts such as cobalt^{II} oximes bearing either H or BF_2 bridges have the same magnetic moment, μ = 1.8−2.1, as noncatalysts **16**, **19**, **20**, and **23**.[140,141] An empirical observation ascribes catalytic properties to all LCo that have four nitrogen atoms coordinated in the

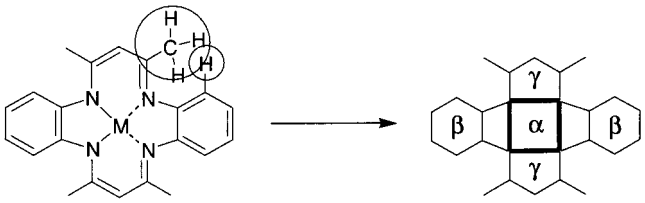
equatorial coordination plane which are incorporated into an extended system of conjugated π-bonds. The equatorial plane may be either open C-shaped or closed O-shaped. Planarity of the macrocycle is important.[131,132] Cobalamin **10** represents such a structure. It has four nitrogen atoms in an O-shaped π-conjugated system.

The active LCo complexes indicated above can be used to test this theory. Porphyrins and phthalocyanines have an O-shaped system which has a more extended π-system than that in cobalamins, but it does not provide a substantial increase in reactivity. It should be noted that the hydrogen bonds of the cobaloxime catalysts are essentially as effective as π-bonds in continuing the effects of delocalization around the macrocyclic ring. This effect has been noted elsewhere.[142] Catalyst **11** comprises an O-shaped π-system. Replacement of one π-bond with a σ-bond in the analogue **13** significantly affects the catalytic properties since both complexes retain their O-shape with π-conjugation. Additional replacement of π-bonds with σ-bonds leads to a complete loss of catalytic properties as chelates **13**, **20**, or **21** indicate. Chelate **22**, cannot be a CCT catalyst because of the absence of interaction between the two π-systems. Chelate **34** is an exception; its molecular structure is similar to **21** and **13**, but it catalyzes chain transfer with a measurable rate. A possible explanation of this phenomenon will be provided in section 3.7.

As with cobaloximes, substituents on the equatorial ligand have only a moderate effect on the value of C_C for the complexes in Table 3. The same is true for substituents on cobalt porphyrins, **1** and **45**−**51** (Table 4). For tetrakis(pentafluoroethylphenyl)-porphyrin−Co^{II} the substituent effect is not clear. The fluorinated porphyrin works moderately for the polymerization of MMA in supercritical CO_2 with chain-transfer constant $C_C = 550$ at 60 °C.[126] Unfortunately, no data on the chain-transfer constant in bulk polymerization are available, so that it is not clear whether this reduced value of C_C is the result of solvent or the presence of a strong EWG such as pentafluorophenyl in the porphyrin macrocycle. Similar experiments with **9c** (Table 2) led to $C_C = 378\,000$, which is 20 times higher than in bulk MMA or in organic solvents.[30] We may conclude at this point that additional experiments are required with different catalysts to allow us to make reliable conclusions.

Complexes **13**−**15** provide interesting additional information on the influence of substituents. Catalytic activity gradually decreases with increasing steric interference between the protons of the methyl groups and the benzylic ring. This steric interference is so high that complex **16** is substantially twisted so that the macrocycle is not planer but rather is "saddle-shaped". According to the crystal structure, cobalt and the four nitrogen atoms are laying in an approximate plane (α), while the aromatic rings (β) are above the coordination plane, and the wings γ are twisted below this plane (Scheme 1). The dihedral angle between the planes β and γ is 43°.[147,148] As a result of the substantial nonplanarity of the molecule, chelate **16** behaves differently from its planar analogues.[149−152]

Scheme 1. Atomic Planes of 15 from Crystallographic Data, Showing the Four-Membered α-Plane, the Aromatic Six-Membered *β*-Planes, and the Five-Membered *γ*-Planes



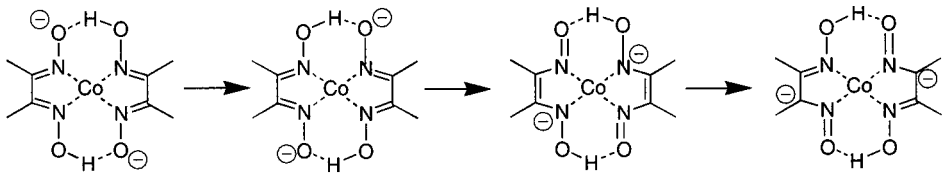
In radically polymerized MMA, LCo **16** does not catalyze hydrogen transfer to monomer but instead catalyzes a termination reaction. This conclusion was reached by comparison of DP_n versus the decrease in rate of polymerization. As mentioned in the Introduction, CCT catalysts do not change the rate of polymerization. In the case of **16**, the rate of polymerization and DP_n decrease linearly with concentration of **16** with a stoichiometric coefficient of inhibition >4. The steric encumbrance of chelate **15** represents an intermediate case between **14** and **16** since it has only two methyl groups instead of four in **16**. Since these methyl groups may twist, only one benzene ring twists slightly from the γ-planes, and complex **16** generally retains the C-shape of the π-conjugation. As a result, **16** shows the properties of a CCT catalyst but its C_C is lower than that of **14** or **34**.

Complexes **35**−**39** also support this conclusion. Catalyst **35** has a planar, C-shaped system of π-conjugation. The three-carbon bridges between the NH and other coordinated nitrogens provide adequate flexibility in coordination so that the entire equatorial ligand is planar. Chelates based on [14]-annulenes are known to exist as strictly planar structures, while bigger/longer ligands, like chelate **39**, can exist in different conformations. Chelates **37** and **38** are not effective catalysts for CTC due to the shortening of the bridge between the two nitrogen atoms from three carbon atoms to two. The two neighboring five-membered rings do not support a planar structure, so that the cobalt and the coordinated nitrogen atoms in these chelates cannot form a perfect plane. A planer molecule cannot be formed at all in the case of **37** with only 12 atoms in the macrocyclic ligand. The observed structures of **37**, **38**, and **39** are reflected in their chain-transfer constants: catalytic activity decreases with increasing nonplanarity of the structure in the series **35** > **39** > **38** ≫ **37**.

Additional understanding of the role of π-conjugation is provided by cobaloximes **6**−**8** and other CCT catalysts with hydrogen bonds which complete the macrocycle (i.e., **32** and **33**). The common feature shared by a π-bond and these hydrogen-bonded systems is their ability to delocalize their electron density.[131,132] Resonance isomers with different bonding of the H or BF_2 bridges to the oxygen atoms allow the electrons to delocalize around the equatorial plane as shown in Scheme 2.

A necessity for a delocalized ring current in CCT catalysts explains the requirement that the equatorial ligand be flat. Chelate **17** would have been a good

Scheme 2. Delocalized Nature of Cobaloximes



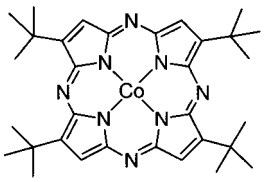
test of this conclusion. It has a 16-member macrocycle that is antiaromatic, and as a result, the equatorial macrocycle is slightly twisted. Hence, it cannot provide ring effective delocalization unless doubly charged to fit the $(4n + 2)$ Huckel requirement. Unfortunately, **17** was tested as the perchlorate salt which makes the results ambiguous.

A phenomenological approach does not explain how the structural features of the CCT catalysts affect the catalytic process. It is obvious that redox properties are involved here. A systematic study of redox potentials and CCT is reflected in Table 5. The higher

Table 5. MMA CCT Chain-Transfer Constants, C_C, and Selected Polarographic Half-Wave Potentials for the Reduction of Co^{II} to Co^{I},[a] $E_{1/2}$, for Cobalt Porphyrins[143]

entry	ligand on Co^{II}	$E_{1/2}$ (V)	C_C	ref
48	tetra(*o*-bromophenyl)porphyrin		1300	139
1	tetramethyl hematoporphyrin IX	−1.06	2400	143
49	mesoporphyrin IX dimethyl ester	−0.98	1800	143
50	tetrakis(*p*-methoxyphenyl)porphine	−0.91	1500	143
51	tetramethyl coproporphyrin IX	−0.90	1500	143
52	tetraphenylporphine	−0.82	1400	143
53	etioporphyrin	−0.79	1100	143
54	protoporphyrin IX dimethyl ester	−0.71	1000	143
2	tetra(*tert*-butylbenzo)porphyrin	−0.70	900	143
55	tetra(pentafluorophenyl)porphine		550	126
56	tetra-*tert*-butyltetraazaporphine		2500	144
57	tetramesitylporphyrin		1500	145
58	tetra(4-sulfonatophenyl)porphyrin		∼1000	146
59	tetra(2,4,6-trimethyl-3,5-disulfonatophenyl)porphyrin		∼5000	146

[a] See also, refs 13, 15, and 17.



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the reduction potential for LCo^{2+} to LCo^{+}, the higher the catalyst activity. While the trend is reasonable, it is important to note the higher values for C_C for the same LCo in this reference. Thus, tetra-*tert*-butylbenzoporphyrin−Co, **2**, has $C_C = 900$ in Table 5 while in another reference $C_C = 300$.[15] Tetraphenylporphyrin−Co, **52**, has $C_C = 1400$ in Table 5 while $C_C = 4000$ elsewhere.[12]

2.3. Non-Cobalt CCT Catalysts

CCT is not limited to macrocyclic complexes of cobalt^{II}. Nonetheless, early experiments with porphyrin complexes of Fe, Ni, V, Sn, Cu, Zn, Mg, Cr, Pd, Pt, and Mn demonstrated no activity.[13,25] Likewise, dioximates of Ni and Cu were found to be inert

Table 6. Chain-Transfer Activity of Organometallic Catalysts in MMA Polymerizations

$[(C_5H_5)Cr(CO)_3]_2$ **60**, 100[153] 160(Sty)	$[(C_5Ph_5)Cr(CO)_3]_2$ **61**, 1000[154]
$(C_5H_5)Cr(CO)_3(C_5H_5)Mo(CO)_3$ **62**, 162[153]	$[(C_5H_5)Cr(CO)_2(PPh_3)]_2$ **63**, 60[153]
$[(C_5H_5)Mo(CO)_3]_2$ **64**, 2[153]	$[(C_5H_5)W(CO)_3]_2$ **65**, 1[153]
$[(C_5H_5)Fe(CO)_2]_2$ **66**, 0.5[153]	$[(C_5Me_5)Fe(CO)_2]_2$ **67**, 9[153]
$[(C_5H_5)Ru(CO)_2]_2$ **68**, <1[153]	$[(C_5Me_5)Os(CO)_2]_2$ **69**, <1[153]

in radical polymerizations.[18] It would be expected that many metal complexes could be catalysts if they are radical-like and have an easily accessible one-electron oxidation. The additional requirement is that they be kinetically labile, because the free-radical polymerization sequence is so rapid that a kinetically inert complex might catalyze one or fewer transfers over the lifetime of a single polymerization chain reaction. Experience with non-cobalt systems is relatively limited. The effects of a series of organometallic complexes were explored in radical polymerizations, and the data is presented in Table 6.[153−155] Most of the MMA polymerizations were carried out in refluxing butanone (80 °C).

Among complexes **60**−**69** only the chromium complexes, **60**−**63**, showed a significant ability to reduce MW. The catalytic process relies upon the dissociation of the dimeric precursors to paramagnetic monomeric organometallic radicals, and the sterically hindered complex, [(pentaphenylcyclopentadienyl) $Cr(CO)_3]_2$, **61**, a derivative of **60**, was more active ($C_C = 1000$ at 100 °C for MMA) than its unsubstituted analogue. The greater steric bulk of the phenyl-substituted **61** increases the dissociation, thereby making the active paramagnetic components more available for the catalytic process.[156] Pentacyanocobaltate, $[(CN)_5Co]K_3$, **70**, has very little activity in the reduction of MW, with $C_C \approx 6$.[157]

3. Mechanism

3.1. Reaction Schemes

Three possible reaction mechanisms for CCT have been proposed. The first two involve metal activation of a substrate to attack by another reactive species, while the third involves sequential reaction of two different species with the metal center. The first was based upon formation of an intermediate complex of the cobalt catalyst with the propagating radical[11,14]

$$R_n + LCo \xrightarrow{k_k} [LCo\cdots R_n] \qquad (10)$$

$$[LCo\cdots R_n] + M \xrightarrow{k_r} LCo + R_1 + P_n^{=} \qquad (11)$$

R_n and R_1 correspond to the polymeric and monomeric radicals respectively, M is monomer, LCo is a cobalt^{II} chelate, [LCo···R_n] is an intermediate complex, and $P_n^=$ is oligomer or polymer with a terminal double bond. Although eq 10 has been observed on numerous occasions, catalyst regeneration (eq 11) is more problematic. It is unlikely that a monomer like methacrylate would abstract a hydrogen atom from a coordinated metal alkyl. It would be expected that hydrogen atom abstraction could be from the α-position, but rearrangement to a coordinated olefin that could be dissociated is possible.[158] This mechanism, deemed to be unlikely, has been explicitly tested and found lacking.[124]

A second proposed mechanism of the CCT was based upon a Michaelis−Menton-type mechanism.[12] This mechanism is typical of enzymatic catalysis,[159] and the rates of CCT have been compared to those of enzymes. It requires the formation of a complex between the catalyst and the monomer (eq 12). The propagating radical then reacts with the complex (eq 13) to transfer a hydrogen atom to the monomer.

$$\mathrm{LCo} + \mathrm{M} \xrightarrow{k_M} [\mathrm{LCoM}] \qquad (12)$$

$$[\mathrm{LCoM}] + \mathrm{R}_n \xrightarrow{k_{tr}} \mathrm{LCo} + \mathrm{R}_1 + \mathrm{P}_n^= \qquad (13)$$

There is little support for the mechanism expressed by eqs 12 and 13. MMA is able to form a π-complex with cobalt porphyrins,[160] but the chain-transfer constant for its formation (1.8 L/mol s) is not high and is much smaller than the observed CCT chain-transfer constants. If the mechanism of eqs 12 and 13 is correct, then reduced concentrations of monomer should disfavor formation of LCoM, resulting in a decrease in the rate of CCT. The chain-transfer constant of the chain transfer is independent of the concentration of monomer.[14,52] The mechanism expressed by eqs 12 and 13 will not be considered further.

A third reaction scheme (eq 14 and 15) encompasses what is the currently accepted mechanism. This scheme was suggested simultaneously with eqs 10 and 12 and calls for the formation of the cobalt hydride, LCoH, as an intermediate species.[161,162]

$$\mathrm{R}_n + \mathrm{LCo} \xrightarrow{k_c} \mathrm{P}_n^= + \mathrm{LCoH} \qquad (14)$$

$$\mathrm{LCoH} + \mathrm{M} \xrightarrow{k_r} \mathrm{LCo} + \mathrm{R}_1 \qquad (15)$$

Since no change in the spectrum of PorCo^{II} was observed during the catalysis, it was assumed that the concentration of PorCoH was very low due to its high reactivity.

Hydrides of cobalt chelates are well documented in inorganic chemistry,[89,163] and cobaloximes received particular attention in the 1960−70s because their chemical behavior was somewhat similar to that of vitamin B_{12}.[85,86,164−171] Although the hydrides of cobaloximes are very reactive, two instances in which $(DH)_2$CoH was isolated have been reported.[88,172] It is believed that in the absence of radicals or monomer, the main mode of decomposition of $(DH)_2$CoH is the bimolecular disproportionation reaction, eq 16.[173−178]

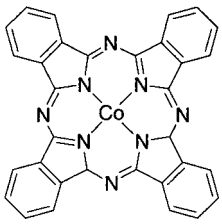
$$2\mathrm{LCoH} \rightarrow 2\mathrm{LCo}^{II} + \mathrm{H}_2 \qquad (16)$$

The chain-transfer constant of about 10^5 L/mol s[172,175] makes it difficult to study the properties of $(DH)_2$CoH. Equation 16 is reversible, and under basic conditions the equilibrium is shifted to the left. LCoH complexes are weakly acidic and are dissociated easily according to eq 17.

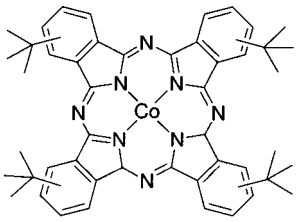
$$\mathrm{LCoH} + \mathrm{Base} \rightarrow \mathrm{LCo}^{I-} + \mathrm{H}^+\cdot\mathrm{Base} \qquad (17)$$

Equations 16 and 17 are known not only for cobaloximes, but also for other cobalt chelates as well. Thus, the addition of bases stabilizes LCoH in its anionic form, slowing the disproportionation reaction in eq 16. The anion which is formally LCo^{I-} behaves as a supernucleophile in S_N2 reactions, reacting with a wide variety of substrates such as acetylenes, olefins, alkyl chlorides, or alkyl bromides.[181,182] The high reactivity of the LCo^{I-} complex together with eq 16 at times makes it difficult to distinguish whether LCoH or LCo^I is the species responsible for a particular reaction. In many cases both LCo^I and LCoH are present in the reaction media simultaneously.

Very stable Co^I chelate complexes are obtained from phthalocyanine ligands (for example, **44** and **71**).



71, Co^{II} phthalocyanine



44, Soluble Co^{II}(tetra-t-butylphthalocyanine)

Cobalt phthalocyanines, PhtCo, can be readily reduced either with hydrazine,[183] with sodium borohydride,[184] or electrochemically.[185,186] In the latter case, PhtCo can undergo five sequential reductions to the pentaanion. All of the negatively charged species have distinct visible spectra. The visible spectrum of PhtCo^I is independent of counterion or solvent. When radical polymerization of methacrylate is conducted in the presence of amides such as dimethylformamide, hexamethylphosphorus tria-

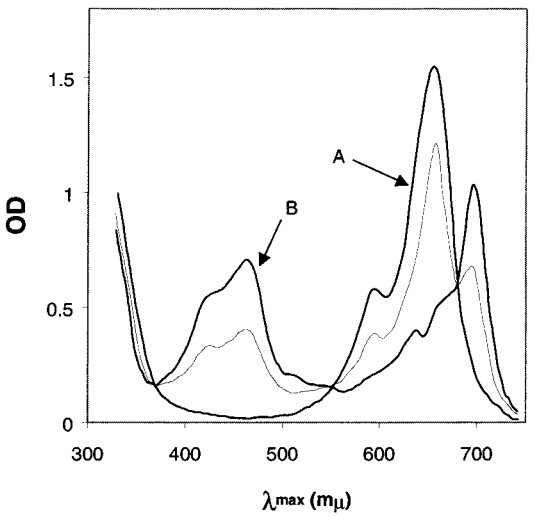


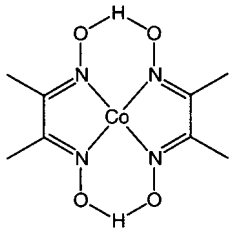
Figure 7. Visible spectra of cobalt phthalocyanine under CCT conditions in HMPA demonstrating the reduction to Co^{I}.[187] A and B are before and after polymerization.

mide, or tetramethylurea, the starting $PhtCo^{II}$ is converted into $PhtCo^{I}$.[187] It is presumed that the tertiary radical reacts with the phthalocyanine to yield the Co^{III} hydride which then dissociates in the presence of base to give Co^{I-}.[188] DMSO also promotes dissociation but is less effective than amides. Since the visible spectra are independent of the method of reduction, UV−vis spectroscopy is an easy and a reliable method to monitor reduction of cobalt phthalocyanine. The three isosbestic points (see Figure 7) indicate that no side reactions occur during the reduction of cobalt phthalocyanine with tertiary radicals.

If a radical polymerization is conducted in bulk methacrylate in the absence of a base, $PhtCo^{I}$ is not formed in detectable quantities. The methacrylate is not responsible for converting $PhtCo^{II}$ into $PhtCo^{I}$. An azo initiator causes reduction even if the methacrylate is replaced with ethyl acetate. Hence, it is the tertiary radicals which convert $PhtCo^{II}$ into $PhtCo^{I}$.

In the case of porphyrins, reduction of Co^{II} to Co^{I} is more difficult. No conditions under which tertiary free radicals would reduce $PorCo^{II}$ into $PorCo^{I}$ at spectroscopically detectable levels were identified. The reduction can be performed electrochemically,[162,189] by treatment of $PorCo^{II}$ with sodium amalgam at room temperature,[190,191] or with borohydride[192−194] at elevated temperatures.[195] In each case, the $PorCo^{I}$ is labile and tends to decompose back to $PorCo^{II}$ and related products when the reducing agent is removed.

Cobaloxime complexes of cobalt, $(DMG)Co^{II}$) **72**, give Co^{I}−cobaloximes $(DMG)Co^{I}$ in the presence of amides by reaction with tertiary free radicals. This



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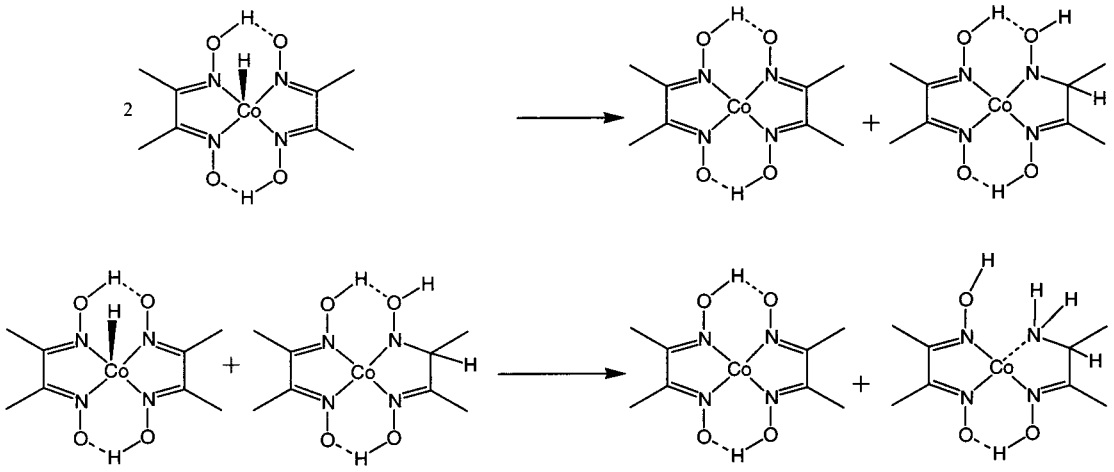
makes them similar to phthalocyanines in initial reactivity, but the resulting $(DMG)Co^{I}$ decomposes slowly with irreversible changes in the equatorial ligand. The rate of $DMGCo^{I}$ decomposition depends on both the equatorial and the axial ligands and ranges from 2 to 0.06% min^{-1}.[187] Among the decomposition products is 3-amino-2-oximinobutane by autoreduction of the dimethylglyoxime ligand.[175−177] Autohydrogenation is very slow in the presence of substrates such as olefin or alkyl halides, indicating that the autohydrogenation is bimolecular as in Scheme 3.

3.2. Hydrogen Atom Abstraction and Catalyst Structure

The process of hydrogen abstraction (eq 14) by LCo from a propagating radical is usually the rate-determining step in CCT. It occurs at diffusion-controlled or close to diffusion-controlled rates indicating that the activation energy for the process must be extremely low. The activation energy of eq 14 depends on the catalyst structure and resulting electronics. For systems such as the less active PorCo with MMA,[196] a significant isotope effect k_H/k_D of about 3.5 was observed.[197] This value of the k_H/k_D

Scheme 3. Autohydrogenation of the Dimethylglyoxime Ligand



effect is similar to the range (1.9−3.3) of kinetic isotope effects observed for hydrogen atom abstraction from a variety of substrates by different metalloradicals.[198−201] It seems reasonable to conclude that hydrogen atom abstraction in CCT occurs by the three-centered intermediate illustrated in eq 18

$$\mathrm{LCo} + \mathrm{R}_n \rightarrow [\mathrm{LCo}\cdots\mathrm{H}-\mathrm{R}_n] \rightarrow \mathrm{LCoH} + \mathrm{P}_n^{=} \quad (18)$$

The kinetic isotope effect would be expected to be smaller or zero if the rate-limiting step involved a concerted β-hydride elimination.[202]

Another reaction of radicals with Co^{II} chelates known to occur at diffusion rates is recombination (eq 19).

$$\mathrm{LCo} + \mathrm{R}_n \xrightarrow{k_{19}} [\mathrm{LCo}-\mathrm{R}_n] \quad (19)$$

In the case of vitamin B_{12}, eq 19 is well investigated and its rate constant $k_{19} = 4 \times 10^9$ L/mol·s for primary radicals.[203] Comparison of this value with the rate constant for methyl radical dimerization of $\sim 10^{10}$ L/mol·s[191] indicates that eq 19 proceeds at diffusion-controlled rates. Newer approaches may provide greater accuracy in the measurement of rates of recombination of free radicals, providing a better understanding of hydrogen atom abstraction (eq 18).[205]

The ratio between the rates of parallel eqs 18 and 19 is an issue of practical importance. Cobalt chelates may be good capping agents in living radical polymerization, LRP.[206,207] This requires that eq 19 be reversible and the forward and backward (eq 20) rates be approximately equal.

$$[\mathrm{LCo}-\mathrm{R}_n] \rightarrow \mathrm{LCo} + \mathrm{R}_n \quad (20)$$

These conditions have been met in a number of systems yielding living radical polymerizations at moderate temperatures.[207−213] For successful LRP, eq 18 should not occur at all and eq 19 is required. For the CCT technologies of this review, the rate of eq 18 should be more than competitive with eq 19, though a low equilibrium level of formation of LCo−R is not detrimental. In addition to choice of proper temperature, solvent, and monomer, the molecular structure of LCo has proven to be the most important factor in achieving effective LRP or CCT. Those LCo that are not effective for CCT should be screened for LRP, though there are many means by which both reactions can fail.

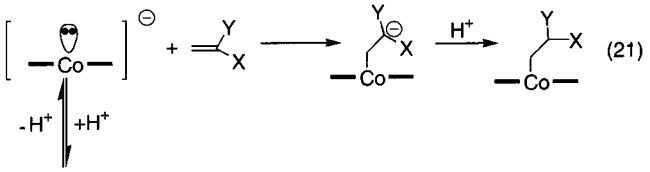
3.3. Hydrogen Atom Addition

Hydrogen atom transfer from the hydride form of the catalyst to monomer (eq 15) is relatively unexplored in comparison with the initial reaction in the catalytic cycle, hydrogen atom abstraction from the growing radical. This is despite the fact that the two reactions are essentially the microscopic reverse, because the substituents on the organic fragment are relatively removed from the metal center. Early investigations of CCT were frustrated by the fact that concentrations of LCoH were below detection limits.[161] The failure to observe LCoH called into question its role as an intermediate species in CCT.

The addition of LCoH to olefinic double bonds is well documented in the chemistry of cobaloximes. Because LCoH has the ability to dissociate to H^+ and LCo^{I-}, both the hydride and Co^{I-} form of the cobalt chelate must be considered in any system where LCoH can be obtained.

The anionic chelates LCo^I are highly reactive nucleophiles, in some cases called supernucleophiles for their reactivity.[214] They readily replace halogen atoms in alkylhalides,[214,215] transalkylate phosphates,[216] add to aldehydes,[217] and add to double bonds.[218] The fragmentation of haloalkylurethanes in the presence of LCo^I was proposed to go through π-olefinic intermediates, but radical chemistry is more likely.[219] The large body of Co^I−chelate chemistry has been reviewed elsewhere, and we refer the reader to available surveys.[43,163,220−225]

For the purposes of this review, it is important to recognize the dual nature of cobalt macrocycle complexes. Both species, $LCo^{III}H$ and LCo^I, can add to double and triple bonds forming alkyl and alkenyl cobalt chelates but the products are different. The Co^{III} hydride reaction occurs in a Markovnikov addition while LCo^I provide anti-Markovnikov products. It is believed that eqs 21 and 22 explain the difference.



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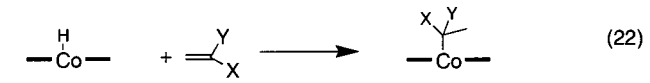
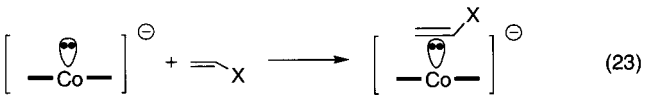


(22)

Substituents X and Y are electron-withdrawing groups. For olefins with strong EWG like CN, the formation of π-complexes (**73**) was observed.[226]

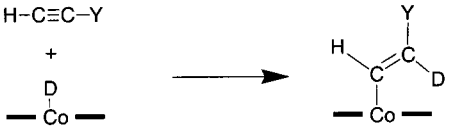


(23)

73

Strong bases ($pK_a > 11$) also convert alkyl cobaloximes and alkyl cobalamins into π-complexes such as **73**. This is usually followed by further decomposition to olefins and alkanes. The stability of complexes such as **73** depends very much upon X and the nature of the axial ligand in the cobalt chelate.[98,218,227−230] Strong nucleophiles such as RS^- or CN^- can cause decomposition of LCo−R as well.[98,231] Under the normal conditions of radical polymerization, Markovnikov organocobaloxime should form whenever the hydride, LCoH, appears in the polymerization mixture. If 1,2-vinylidene monomers are being polymerized, then thermally unstable *tert*-alkyl-cobaloximes are obtained. These species are expected to undergo homolytic Co−C cleavage to yield tertiary radicals.

An alternative mechanism calls for hydrogen atom transfer by the reverse of eq 14 with no organometallic intermediates. Attempts to distinguish between these two possible pathways of hydrogen addition employed deuterium labeling. Stereoselectivity in the addition of LCoH to double and triple bonds was observed. Early work indicated Co−D cis addition to olefins and acetylenes.[232] Later experiments showed



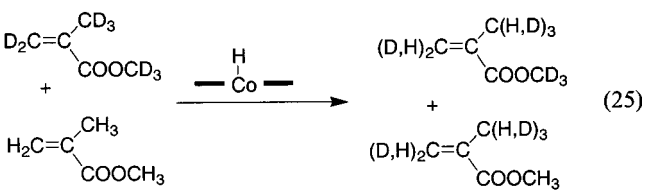
(24)

a maximum of ~70% cis addition.[233] Cis addition falls to ~60% when octaethylpoprphyrin−CoD reacts with phenylacetylene.[234]

It is important to carefully control reaction conditions during experiments with LCoH and LCoD, particularly the availability of exchangeable hydrogen atoms. LCoD can be prepared using $NaBD_4$. Borohydrides are known to change the acidity of the reaction medium during the course of the reduction reaction, and this can have a direct affect on the outcome of the reaction. An alternative approach to Co−D complexes is through the decomposition of deuterated alkylcobaloximes. D/H exchange with CH_3OD is negligible, but the synthesis of the deuterated organometallic precursor is itself a problem.

Steady-state, free-radical methods of LCoD generation were developed.[197] The methods are versatile and work for LCo like cobalt porphyrins that are not readily reduced by borohydrides. The use of tributyltin hydride has also been reported.[235] The initial approach employed AIBN-d_{12}. Using this deuterated radical source, cis addition of the resulting LCoD was demonstrated to be the predominant mode of reaction for maleic anhydride and other cyclic olefins such as cyclohexene and 2,5-dihydrofuran. Selectivity depended upon temperature, and this important feature will be discussed below. Unfortunately, AIBN has a limited thermal operating window of 50−70 °C. Lower or higher temperatures would require the nontrivial synthesis of different deuterated azo initiators. To circumvent this problem, a second steady-state free-radical approach was developed.

When perdeutero-MMA was copolymerized with perhydro-MMA in the presence of AIBN and a CCT catalyst under conditions that favor formation of MMA-dimer, it was observed that the product had undergone hydrogen/deuterium scrambling. Unreacted monomers in the reaction mixture were also scrambled.



(25)

It was clear that rapid hydrogen/deuterium exchange was occurring in a radical cage[236] involving LCoH/LCoD and MMA before the monomeric radical escaped the cage to propagate polymerization in solution. The suggestion was confirmed by employing perhydro azo initiator and MMA-d_8. The unsaturated molecule 2,5-dihydrofuran was added to trap the intermediate. As expected, the isolated tetrahydrofuranyl cobalt complex was deuterated in the *cis*-vinyl position. Unexpectedly, MMA-d_8 was discovered to be a highly efficient deuterium donor. A 2-fold excess of MMA relative to LCo was enough to convert LCoH into a LCoD before reaction with dihydrofuran. Using these methods, the results shown in Figure 8

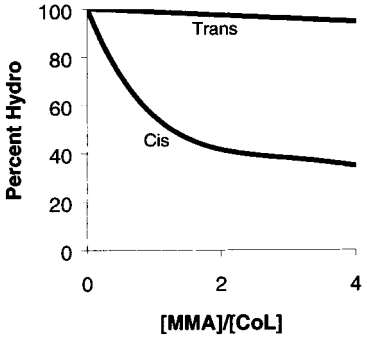
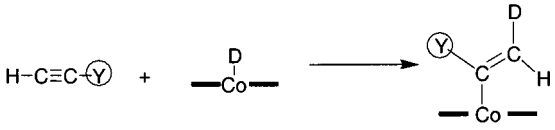


Figure 8. Hydrogen/deuterium dependence at the β-carbon atom of (TAP)Co−(3-tetrahydrofuranyl) on the concentration of MMA-d_8 relative to cobalt.[197]

were obtained. Thus, to obtain LCoD, the azo initiator appropriate for the desired temperature is combined with a small portion of MMA-d_8.

Stereoselectivity of the addition of LCoD to olefins is very dependent upon the temperature. The most probable reason for diminished selectivity is the thermal lability of the Co−C bond at temperatures above 50 °C for all olefins studied to date. In the case of maleic anhydride, the initial product is LCo−succinylanhydride. Under more forcing conditions in the presence of excess AIBN, formation of a new organometallic species, LCo−succinylanhydride−$C(CN)(CH_3)_2$ was detected. Formation of the new adduct almost certainly resulted from Co−C bond cleavage, and this same cleavage would lead to stereochemical inversion. At temperatures less than 50 °C, additions are somewhat more stereoselective. Nonetheless, maleic anhydride was the only olefin to give quantitative cis addition at lower temperatures. Other olefins displayed some trans addition even at these temperatures. Thermal isomerization results in loss of selectivity at longer reaction times, but even the product initially formed displays some trans isomer, and thermal instability of the Co−C bond cannot explain this observation. There must be some inherent lack of selectivity.

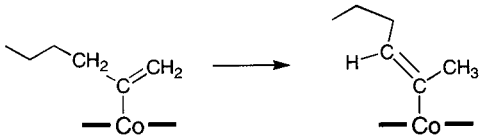
In contrast to olefins, the addition of acetylenes to LCoD shows clear trans addition as in eq 26.



(26)

The reaction proceeds well even in the presence of a 100-fold excess of MMA-d_8 to generate the label. The addition of the cobalt deuteride to 1-hexyne or

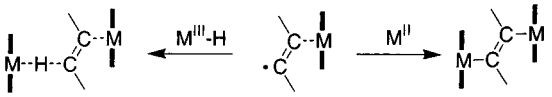
5-hexynenitrile displays Markovnikov regioselectivity and trans (anti) stereoselectivity. The high conversion of the Co^{II} to vinyl $cobalt^{III}$ porphyrins allowed labeling using AIBN-d_{12} as a source of (TAP)CoD. Unexpectedly, the incorporation of deuterium into the axial vinyl substituent on cobalt was dependent upon the concentration of the acetylene, with only 40 atom-% *trans*-vinylic deuterium addition at 0.04 M 1-hexyne increasing systematically to 90 atom-% at 1 M. The deuterium content of the product increased during the course of a reaction at fixed acetylene concentration with no deuterium incorporation at the *cis*-vinylic site occurring during these experiments. The unaccounted deuterium was lost to an unknown side reaction. The presence of a large excess of exchangeable MMA-d_8 overcame the unknown reaction and provided a high level of deuterium incorporation in the *trans*-vinyl position. In some cases, isomerization (eq 27) of the initial product was observed.



(27)

The source of trans stereoselectivity for Co−H addition reactions to acetylenes while olefins are generally cis is unclear. Cis[237] and trans[238] additions of acetylenes are known in platinum chemistry, and radical intermediates are thought to play a role in some insertions.[239] Cis additions indicate concerted insertion reactions, while trans additions are indicative of radical pathways. Sterically demanding acetylenes can lead to a reversal of regio- and stereochemistry.[208]

Species such as **74** and **75** could be intermediates in the trans addition of cobalt hydride to acetylene.

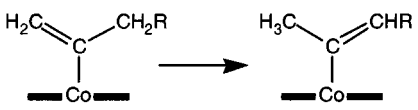


(28)

74 **75** **76**

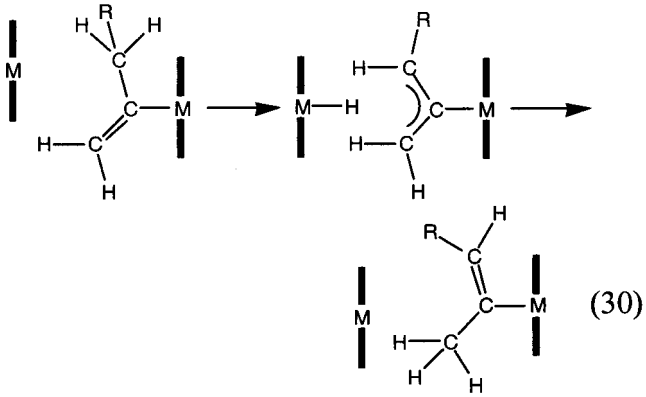
Bridged species such as **76** are well documented in rhodium porphyrin chemistry.[240,241] An acetylene bonded to one metal-centered radical is presumed to be trapped by addition of a second metal-centered radical. Lower bond dissociation energies of cobalt relative to rhodium would disfavor species such as **76** and facilitate the reaction with metal−hydride intermediates to form a trans product.

Involvement of a second porphyrin in the reaction of CoH with acetylenes was inferred from the inverse relationship between the rate of eq 29 and the steric bulk of the porphyrin molecule.[5b]



(29)

Unimolecular isomerization could occur by a Co−C bond cleavage to yield radical intermediates that isomerize. The rate of isomerization of the coordinated vinyl would be expected to be higher for sterically hindered porphyrins that favor homolytic dissociation, but this does not fit the observations. An alternative unimolecular mechanism would involve a concerted 1,3-hydrogen shift, but it is difficult to explain why a relatively remote terminal group of the axial ligand would have an effect on the rate of isomerization as observed. The decrease in the rate of isomerization for a coordinating nitrile substituent versus a noncoordinating methyl substituent is explained by a bimolecular catalyzed reaction as in eq 30.



(30)

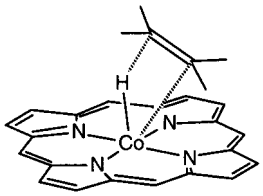
The reactive, unsaturated site of an incoming porphyrin molecule would be filled by the nitrile substituent preventing interaction with the α- or *β*-sites of the vinylcobalt porphyrin molecule. The methyl group would have no such interaction, allowing the porphyrin to approach in an active state. Such a Co^{II}-catalyzed isomerization of an $allylcobalt^{III}$ is precedent by cobaloxime chemistry.[242] Kinetic investigation of the isomerization indicates that the rate of isomerization of the primary acetylene adduct to the secondary product early in the reaction is several times the rate late in the reaction when Co^{II} would be depleted, supporting the intermediacy of a species such as **74**.

3.4. Alternative Mechanisms for Olefin Reactions with Co^{III}–H

The chemistry of vitamin B_{12}-catalyzed rearrangements has been a subject of intensive investigation.[243] Although there is much to support the free-radical nature of such rearrangements, there is a growing body of evidence which favors nonradical mechanisms under at least some conditions.[244−246] Polar effects are known to play an important role in the addition of free radicals to double bonds.[247] Radicals can form relatively stable adducts with a variety of salts,[248] phosphines,[249] and conjugated double bonds.[250] Additionally, radical species can undergo one-electron oxidation/reduction when reacted with metals or olefins,[251] and these one-electron transfers can be quite reversible.[252] For these reasons, radical, ionic, or electron-transfer mechanisms cannot be ruled out. A given metal complex may be able to convert radical species into ionic intermediates and back. Because of this complication, the origin of some selectivities may be based on the limiting step of a multistep process.

Experiments with model compounds demonstrated the exceptional importance of the π-system in molecules involved in chain-transfer catalysts. Cobalt chelates without planar, extended conjugated π-systems are not active in chain-transfer catalysis.[132] One possible explanation of this could be the necessity of hydrogen atom migration from cobalt to ligand during the catalysis. Disruption of the conjugation by the hydrogen atom migration should be less in an extended π-system.

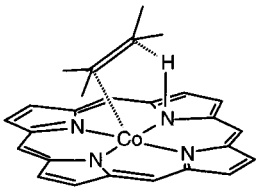
Concerted insertion of an olefin into a CoH bond or its microscopic reverse, β-hydride elimination, involves the intermediate species **77**.



77

The availability of only one coordination site due to the large rigid equatorial ligand of the cobalt porphyrin macrocycle would appear to make such an intermediate unlikely. Viewed as a transition state with a large component of C−H bond formation, the Co−C bond formation would occur later in the process. In the extreme of complete C−H bond formation prior to Co−C formation, the intermediate is indistinguishable from a radical mechanism.

The cobalt−hydride intermediate has not been isolated and is virtually undetected. Cobalt hydride reaction with an olefin by first migrating the hydrogen atom from cobalt to a porphyrin nitrogen atom (**78**) or carbon atom (**79**) is precedented by the isomerization of a benzylcobalt chelate. In that case, the benzyl migrates reversibly from the cobalt to the carbon atom of the equatorial ligand.[253]



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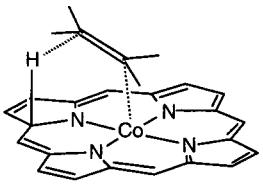


79

It is also reported that alkyl groups in N-substituted Ni and Pd corroles can migrate from pyrrolic nitrogen to the β-carbon atom of the pyrrolic ring.[254] The intermediate is also precedented by complexes bearing partially hydrogenated cobaloxime ligands produced by exposure of the complexes to molecular hydrogen.[177] Migration of organic substituent from metal to nitrogen and addition of acetylenic substrate to both metal and macroligand have been reported in several dozen publications.[255,256] Support for a possible role for hydrogen atom migration from the metal atom to a macrocyclic ligand is provided by the coexistence of a normal rhodium phthalocyanine hydride and its isomeric form in which the hydrogen atom is located on one of the ligand nitrogen atoms.[257] Hydrides of cobalt chelates are known to be less stable than those of rhodium, so it is likely that a hydrogen atom would undergo migration from cobalt to ligand at rates faster than those in rhodium phthalocyanine. Mechanisms based upon these intermediates or transition states are plausible alternatives to the caged radical pair, though the intermediates would have to be very short-lived because the rates of the catalytic chain transfer are so high. Rapid, reversible migration of the hydrogen atom between cobalt and ligand could be responsible for the poor stereoselectivity of cobalt hydride addition to the double bond of cyclopentene at low temperatures when thermal isomerization of the Co−C adduct is known to be negligible.[208] If a Co−H transfer is not stereoselective and a ligand hydrogen atom transfer is stereoselectively cis, then the overall stereoselectivity of cyclopentene addition to $LCo^{III}H$ would reflect the ratio between the concentrations the isomers, CoH, and LH.

An important feature of the LH form of the hydride is that it contains a Co^{III} bearing a very open coordination site for reaction with nucleophiles. There are several publications on the unusual reaction of "naked" $cobalt^{III}$ in porphyrins with acetylenes and olefins.[256h−j,258] This could also explain the trans addition of the hydrides to acetylenes. A charge-transfer intermediate in the reaction of the LH isomer with an acetylene or alkene could explain the difference in behavior of substituted versus unsubstituted olefins. If the above explanation is correct, then it would require essential equality between the energies of the Co−H and L−H complexes. Parameters such as solvent properties could shift the equilibrium concentrations of the two isomers of the hydrides, leading to apparently different results in the same reaction and explain poor reproducibility in stereoselectivities.[232,233]

The role of protic intermediates was recognized in the very earliest work on $hydridocobalt^{III}$ chelate reactions.[259] In basic solutions, H/D exchange was relatively fast, while neutral or acidic conditions reduced the rate significantly.[230,260] The chemistry is associated with $hydridocobalt^{III}$ and the deprotonated anionic complex which is formally $cobalt^{I}$. Under basic conditions, the regiochemistry is reversed with acrylonitrile giving the primary alkyl, $Co^{III}CH_2CH_2$-CN.

Caution is required in extrapolating the conclusions from one particular set of reactants and conditions to other closely related systems. The chimeric nature of CoH, reacting as a free-radical or an ionic species, can depend both on the nature of the equatorial ligand and on the trans substituents, particularly if migration of the hydrogen atom over the surface of the equatorial ligand plays a role in the insertion reaction. In this case, the structure of the equatorial ligand rather than the redox potential of the metal center may control the course of the reaction.

The addition of double bonds to $hydridocobalt^{III}$ chelates is clearly dependent on the structure of organic substrate. Generally, electron-withdrawing

substituents promote cis addition while electron-donating substituents lead to loss of selectivity in the reaction. It is likely that olefins and acetylenes react with CoH by different mechanisms and parallel reactions may occur.[261]

3.5. Living Radical Polymerizations

The phenomenon of living polymerization is observed whenever propagation and reversible termination are significantly faster than any process for irreversible termination. The primary route of termination in free-radical polymerizations is bimolecular in nature. If the persistent radical effect can be employed to reduce the instantaneous concentration of active radicals in solution at a given time, then bimolecular termination can be greatly reduced. This is done by establishing an equilibrium between active and dormant radicals. The resulting polymerization is living in that M_n increases in direct proportion to the conversion of monomer. The molecular weight distribution in resulting living radical polymerization (LRP) is narrow, and it is possible to prepare a number of desirable polymer architectures such as block copolymers and end-functional polymers.

Under certain conditions, some poor CCT catalysts are potentially good candidates for living radical polymerizations, LRP, if the factor limiting the CCT is formation of a stable metal alkyl species, $LCo^{III}-R$, which removes active cobalt^{II} from the reaction.[262−264] This stable species is not an intermediate in the CCT reaction but rather represents a side reaction.[123] This has been observed for a variety of olefins, actually allowing isolation of the Co^{III}–alkyls[262] and determination of the Co−C bond strengths and kinetics of Co−C bond homolysis of several of these species.[265−269] The strong ring currents of porphyrins and phthalocyanines[270] make the use of NMR spectroscopy particularly advantageous. In many cases involving catalysts **48**−**59,** retardation of polymerization was observed, thereby complicating the overall mechanistic picture. Retardation has also been reported for porphyrin complexes of metals other than cobalt, with the retardation increasing in the order Zn ≈ Ni < Pd < Cu ≈ Mn ≈ Cr.[17] This retardation indicates that these porphyrin complexes may participate in other reactions with the propagating radical including LRP since retardation is an inherent feature of LRP,[271] but additional experiments are required to discover the origin of the retardation. This effect may sometimes be referred to as the "persistent radical effect".[272−276]

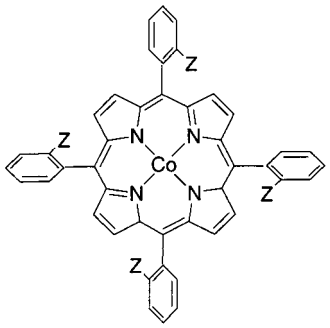
In selected cases, it is possible to convert effective CCT catalysts to species suitable for LRP by incorporating special substituents into the design of the equatorial ligand. Above, we demonstrated that substituents usually have little effect on CCT chain-transfer constants. These limited effects are generally deemed to be electronic in nature. There are several special instances of ortho-substituted phenyl substituents having a substantial influence on C_C. Ortho-substitution on phenyls can play a significant role by preventing the phenyl rings from being coplanar with the macrocycle through steric interactions such as those discussed above with chelate **16** as an example. The difference between **16**, where π-delocalization was interrupted, and ortho-substituted phenyls in the macrocycle is that they force the phenyl to be perpendicular to the macrocycle plane, positioning the ortho-substituents directly above or below the plane of the macrocycle. This creates a steric obstruction to the propagating radical as reaction with the cobalt center takes place.

Table 7. CCT in Polymerization[a] of Bulk Styrene Catalyzed by Porphyrins 80[144]

entry	substituent, Z	C_C	phenyl−Z bond length (nm)
80a (50)[b]	H	2150	0.108
80b	OMe	1530	0.135
80c	Me	1000	0.152
80d	Cl	610	0.170
80e	Br	550	0.185

[a] Bulk MMA, 60 °C. [b] 4-Anisyl.

Porphyrin molecules provide a good example of this effect.[144] In Table 7, a clear connection between the size of the ortho substituents and the chain-transfer constant, C_C, is observed. The electronic effects of the substituents are less important because methyl and chloro have similar C_C but significantly different electronic effects. According to X-ray data, porphyrins such as **80** are so restricted in rotation of the phenyl rings that four atropo-isomers can be easily separated by preparative chromatography.

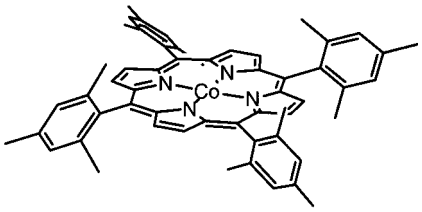


80

The substituents, Z, can be located both below and above the plane. Both sides of the porphyrin plane are equivalent, so the purely statistical ratio between concentrations of the atropo-isomers (above the plane/below the plane)—(0/4):(1/3):(2/2)—is 1:4:3. About 12% of all the porphyrin molecules will have one completely unsubstituted side (the other side being tetrasubstituted) having the same steric exposure as an unsubstituted porphyrin. Experimentally, the methoxy-substituted porphyrin displayed 8% of the (0/4) atropo-isomer, which is very close to the expected value based upon populations of active species alone.[277] Hence, it would be expected that at most 10% of the ortho-substituted phenyl porphyrins **80** could provide full activity regardless of the size of the Z-substituents. The concentration of atropo-isomers (1/3) and (2/2) are approximately equal, so if the (2/2) isomer completely blocks radical approach, then C_C should be about one-half of that of the unsubstituted porphyrins. From Table 7, one may conclude that having one methyl or one methoxy group is not enough to block the cobalt reaction with the propa-

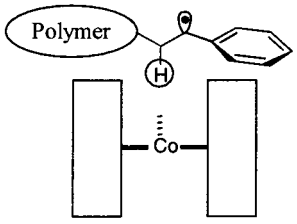
gating radical while one bromo substituent is. Even taking tetrakis(*p*-methoxyphenyl)porphyrin−Co (C_C = 2200[144]) as an electronically corrected, ortho-unsubstituted reference catalyst, one may draw the same conclusion.

The cobalt complex of tetrakis(mesityl)porphyrin, **57**, is one of the most commonly utilized sterically hindered porphyrins because there are no atropo issues, with each side of the macrocycle having four ortho-substituents.

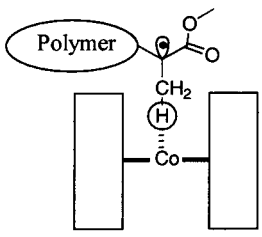


57

In the polymerization of MMA, **57** is one-half as effective as its unsubstituted analogue, tetraphenyl porphyrin cobalt, with their respective C_C being 1500 and 4000.[145] In contrast, **57** was found to be completely inactive in styrene polymerizations, with $C_C < 1$, while **80c**, a mono-ortho-unsubstituted analogue, has C_C = 1000 (Table 7). This is an unusual result because the polystyrenic radical is a secondary radical while the polyMMA radical is tertiary and more sterically hindered. The ortho-methyl substituents in **57** create a fence around cobalt so that the cobalt atom is sitting at the bottom of a pocket. It is difficult to explain how a tertiary polyMMA radical reacts with such a deeply hidden cobalt while the polystyrenic radical cannot. The nature of the resulting product suggests the answer. The secondary styrenic radical is too bulky to insert its β-hydrogen atom into the pocket of **81**.[145] In contrast, free radicals having a β-methyl group, like the PMMA propagating radical, can extend the methyl group into the "pocket" of porphyrin **77**, allowing hydrogen atom transfer to cobalt as shown in **82**.

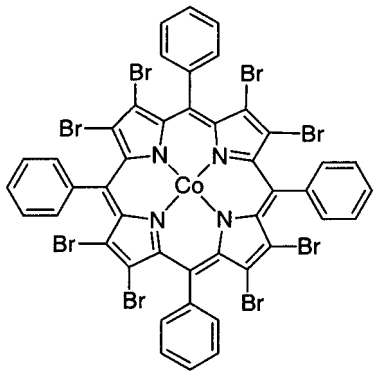


81



82

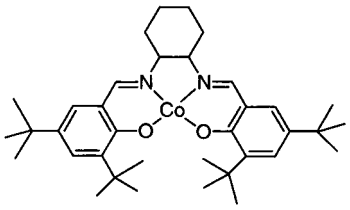
Careful tuning of steric and electronic effects can lead to the elimination of CCT, allowing living radical polymerization to dominate.[207,278] Acrylates can be polymerized by the LRP mechanism using **57** as a capping agent, and there is no hydrogen atom abstraction leading to catalytic chain transfer. Another reported successful cobalt porphyrin as a capping agent for LRP in polymerization of acrylates is when the octabromotetraphenylporphyrin Co derivative, **83**, is employed; the temperature for active LRP is reduced from 80 to 30 °C.[279,280]



83

Porphyrin **83** is substantially twisted due to unfavorable steric interactions between bromine atoms and the hydrogen atoms of the phenyl substituents.[281−283] Like complex **16**, **83** is saddle-shaped. The nonplanarity of the LCo structure reduces the hydrogen atom abstraction capability of **83**, making it very good for capping propagating radicals without side reactions.

Chelate **84** exemplifies another approach in the construction of cobalt chelates suitable for LRP.



84

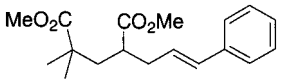
The replacement of one or more of the equatorial chelating nitrogen atoms with atoms of other elements reduces the π-conjugation to the extent that CCT does not occur. The attempted use of **84** for LRP led to side reactions, but it is not obvious that the side reaction was hydrogen transfer.[284]

One additional example of LRP in the presence of LCo will be discussed below (see section 4.5 on acrylates).

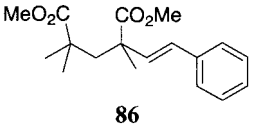
The photochemistry of cobalt−carbon bonds is well established[285−288] and can be utilized to initiate a living radical polymerization in systems where the monomer leads to stable Co^{III} alkyl species.[289,290] Photolysis of the Co−C bond liberates an active radical species which adds monomer before being retrapped by the cobalt center. Another photon is required after each trapping event. Useful end group functionality (−OH, −COOH, −COOR, −halogen, or −CN) is introduced through the choice of starting cobalt complex. The molecular weight of the polymer increased with conversion, and products with narrow molecular weight distributions were obtained as expected for a living system. Polymers with block, star, and radical−block architectures are possible. Similar results can be obtained with $rhodium^{III}$−alkyl porphyrin complexes. It is possible to start with Rh^{II} and obtain an alkyl-bridged rhodium dimer when employing acrylates. When the sterics are undemanding, the bridge consists of two carbon atoms, but

when steric demands are increased, a four-carbon bridge is obtained through head-to-head dimerization of the acrylate.[291]

Photochemical reactivation of methacrylate oligomers has been observed.[292] For instance, MMA dimer was metalated with a cobaloxime. The preformed methylene-bound product was photolyzed in the presence of styrene yielding **85** rather than the expected **86**. The poor yield of **85** is not unexpected, considering the high reactivity of the methylene-based radical species that would be generated.



85



86

It would be expected that the highly reactive methylene-radical intermediate would react quickly with any available styrene.

In concluding this section, the criteria described above for the identification of good CCT catalysts are also useful in the identification of good capping agents for LRP. The extended, planar, π-conjugated system of good CCT agents should be reduced for good LRP agents. Substitution of two of the four nitrogen atoms in the equatorial chelate in good CCT catalysts leads to good LRP catalysts. Of course, in the search for good LRP capping agents, it is important that the properties of the metalloradical be tuned to the properties of the propagating radical. More reactive propagating radicals should be paired with less stabilized metalloradicals, i.e., in going from methacrylates to acrylates, the LRP end-capping metalloradical should have fewer nitrogen atoms in the coordination plane and a less extended π-system.

3.6. Catalytic Inhibition of Polymerization

Catalytic inhibition, CI, of polymerization was discovered almost simultaneously with CCT.[13] In searching for the best CCT catalyst, the solubility of the catalyst is one of the important issues. Cobalt chelates with large planar ligands are poorly soluble in the desired monomers and common organic solvents such as acetone and dichloroethane. The solubility can be improved by incorporating more substituents into the equatorial ligands of the complexes, but this approach requires substantial synthetic effort. The easier approach is to use amides and DMSO as solvents because these solvents will dissolve most of the complexes both as their electroneutral forms and as salts.

The testing of cobalt phthalocyanine in radical polymerization was first conducted in quinoline solution because it was known to be inert for radical polymerization. Surprisingly, instead of CCT, catalytic inhibition was observed.[14] Inhibition is generally considered to be an undesirable event in polymerization. In those few cases when inhibition of polymerization is required (for instance, monomer stabilization), less expensive noncatalytic inhibitors worked well. As a result, the phenomenon of CI did not attract much attention.

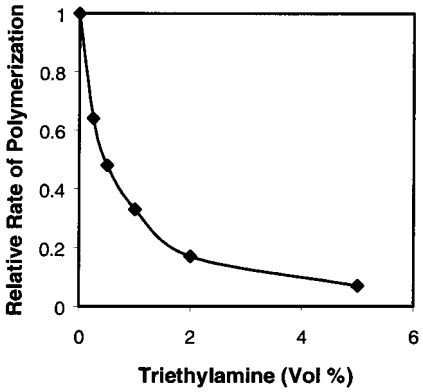


Figure 9. Dependence of CI on added triethylamine.

Subsequently, CI was observed in polymerization of MMA with high concentrations of cobaloximes,[77,293] phthalocyanines,[14,136,294,295] and porphyrins.[295] CI is observed only when the cobaloxime was in the 2+ oxidation state and can catalyze chain transfer.[296] Thus, CI is a phenomenon that is closely connected to CCT. The first explanation involved a "hydride" (as in eq 31), where P_n is a polymer obtained from the propagating radical which has been terminated by hydrogen atom donation by $Co^{III}-H$.[161]

$$LCo - H + R_n \rightarrow LCo + P_n \qquad (31)$$

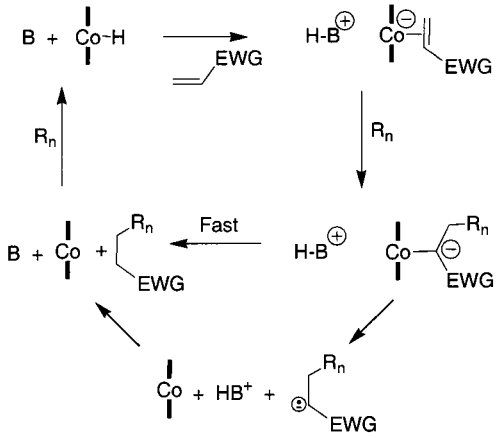
The second explanation of CI was that the polymerization rate constants are dependent upon the radical DP for DP < 8, so that retardation occurs due to the higher value of k_t for small radicals.[44] As indicated above, the propagation rate constants actually increase at lower molecular weights. There are two additional reasons to believe that k_t cannot be responsible for the CI.

First, low oligomers of the same DP can be obtained with different catalysts, but the observed decrease in the rate of polymerization is different. For cobaloximes the decrease is substantial, while cobalt porphyrins do not reduce the rate of polymerization[13] except in the very initial stages when some adduct between the propagating radical and cobalt porphyrin forms.[52] Retardation should be independent of the type of the catalyst if it were dependent upon k_t.

Second, for cobalt phthalocyanines, CCT and CI are dependent upon the addition of quinoline.[136,294] Addition of low concentrations (0.1−0.001 M) of quinoline reduces the rate of CCT by cobalt phthalocyanines. Higher concentrations of quinoline increased CI and slowed CCT, converting CCT catalysts into CI catalysts. These observations were interpreted in favor of eq 31.

In copolymerization of acrylonitrile and styrene, 1−5% of added nitrogen base may promote MW reduction.[297] Several bases including pyridine, triethylamine, and DABCO convert CCT catalysts into CI catalysts in the polymerization of MMA,[298] suggesting that the bases are proton acceptors converting $LCo-H$ or $LCo-R_n$ into a π-complex of LCo^I with monomer. Figure 9 shows the dependence of the

Scheme 4. Effect of Base in Catalytic Termination



inhibition on added triethylamine in an MMA polymerization at 60 °C with tetra(anisyl)porphyrin (2×10^{-4} M).[139] Interestingly, the noncoordinating molecule DABCO behaves the same as triethylamine, indicating that coordination as a ligand is not important. The resulting complex may trap the next radical by converting it into an anion, as in Scheme 4. Triphenylphosphine behaves similarly to the amines. At amounts equimolar to the cobalt, it may increase the rate of CCT, while higher concentrations decrease CCT by facilitating CI.[78,298] Whether phosphines are basic enough to participate in Scheme 4 remains an open question.

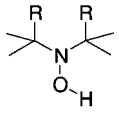
In addition to cobalt complexes, other compounds are potentially able to catalyze the termination of growing radical chains. As a result of their free-radical nature, nitroxides (T$^{\bullet}$) and other capping agents in LRP are potentially able to abstract hydrogen atoms from propagating radicals through eq 32

$$T^{\bullet} + {}^{\bullet}R_n \rightarrow T{-}H + P_n^{=} \qquad (32)$$

The ability of nitroxides to abstract hydrogen atoms from various organic substrates has been known since the initial discovery of nitroxides.[299] Since the coupling eq 33 is much faster reaction than eq 32, eq 32 may seem to be of little consequence under the conditions of LRP.

$$T^{\bullet} + {}^{\bullet}R_n \rightarrow T{-}T_n \qquad (33)$$

Nonetheless, the probability of termination eq 32 may be important in two circumstances. First, during LRP, the probability of eq 32 increases with each forward and reverse reaction, eq 33, leading to the accumulation of polymer with unsaturated ends with time. Second, low MW free radicals may be more prone to eq 32 than higher MW radicals because of the dependence of reactivity on molecular weight. Nitroxide may react with the propagating radicals of styrene by eq 32 at significant rates.[300] Thus, at 90 °C, $k_{32}/k_{33} = 0.1{-}0.3$. As a result of hydrogen atom transfer, hydroxylamines, **T**−**H**, are formed.



T-H

These hydroxylamines terminate propagating radicals by eq 34.

$$T{-}H + {}^{\bullet}R_n \rightarrow T^{\bullet} + P_n \qquad (34)$$

The reaction rate constants can be 15−35 L/mol·s depending upon the molecular structure of the nitroxide. The combination of eqs 32 and 34 constitutes a catalytic cycle of CI by hydrogen atom transfer.

3.7. Catalyst Poisons and Other Adverse Reactions

An understanding of side reactions is an important part of any commercial process. The level of understanding is an indicator of the maturity of the process. In the first excitement of a new discovery, side reactions are far from the researcher's mind, but practical implementation of a technology generally uncovers everything that can go wrong. Transition-metal complexes involved in free-radical polymerization may be attacked by the highly reactive free radicals. Free radicals can add to double bonds of porphyrins.[301] Metal-free porphyrins readily react with secondary propagating radicals (Scheme 5) such as those of acrylates yielding the chlorin, **89**. Further addition yields the bacteriochlorin structure, **90**.

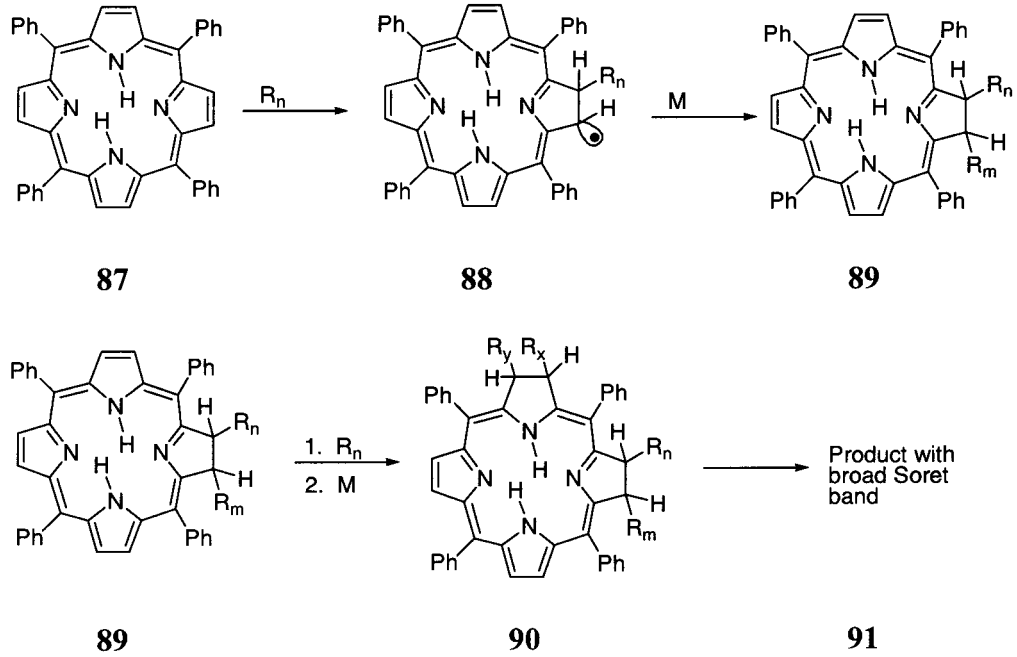
The rates of radical addition to the double bonds decrease from **87** to **90**, allowing the process to be observed stepwise. Under extreme conditions, it is possible to obtain species where the cyclic π-conjugation is completely destroyed in some final uncharacterized product **91**.

In Scheme 5, the radicals derived from acrylates and vinylpyrrolidone (VP) give products that are spectroscopically similar. VP is the more interesting monomer because it provides a polymer with solubility different from that of the porphyrin. Porphyrins are generally insoluble in water and methanol, but after "copolymerization" with VP, they become soluble in water and most organic solvents. The high conversion polymerization of VP with porphyrin results in a cross-linked material from which porphyrin does not leach into solution, indicating that the macrocyclic radical **88** actually propagates polymerization rather than trapping the excess of propagating radicals.[302]

Metalloporphyrins behave differently, and the mechanism is dependent upon the nature of the metal.[301] In addition to the formation of M−C adducts, there are other unspecified reactions with metalloporphyrins which have not been characterized spectroscopically. It is presumed that Scheme 5 may be included in the processes that affect CCT in the case of vinylic monomers that yield a secondary propagating radical.

In the chemistry of cobaloximes, the addition of radicals to the double bonds of the equatorial ligand

Scheme 5. Radical Attack on Tetraphenylporphyrin



87 **88** **89**

89 **90** **91**

was reported.[253] The benzyl radical is involved in an equilibrium between cobalt and carbon-centered adducts.

Oxygen may substantially reduce the catalytic activity of porphyrin CCT catalyst.[75] First, the peroxo radical, $R_nO_2^{\bullet}$ forms as in eq 32.

$$O_2 + {}^{\bullet}R_n \rightarrow {}^{\bullet}O_2R_n \qquad (35)$$

The peroxo radical then oxidizes the cobalt porphyrin with the formation of several products with a rate constant of 7000 M^{-1} s^{-1}, typical for peroxo radicals in their reaction with cobalt^{II} complexes. In addition to the alkylperoxoCo^{III}−porphyrin, **92**, in eq 36, there is concomitant formation of a Por′Co species in which the porphyrin ligand has been modified.

$$R_nO_2^{\bullet} + PorCo^{II} \rightarrow PorCo^{III}-O_2R_n + Por'Co \qquad (36)$$

Reaction of the porphyrin ligand leads to degradation of the Soret band and reduction of ring current in NMR spectra after prolonged polymerization in the presence of air.[75] The concentration of Por′Co species increases with time during a polymerization, possibly because of multiple reactions of peroxo radicals with the porphyrin macrocycle.

The BF_2-bridged cobaloximes probably behave similarly to cobalt porphyrins, but detailed studies are not available. The H-bridged cobaloximes are more reactive toward oxidation than cobalt porphyrins or phthalocyanines; their Co^{II} complexes are oxidized immediately by dioxygen upon contact. The increased oxygen stability of Co^{III} BF_2-bridged complexes explains why they are preferred for industrial applications. The alkyl−Co^{III}−cobaloximes, where the alkyl radical is more stable than methyl, decompose at elevated temperatures to yield the active Co^{II} derivatives. Studies indicate that the oxidized Co^{III} species are reduced by propagating PMMA radicals.[77,188,303,304] When the monoanionic ligand, A, is halogen in a Co^{III}−cobaloxime (eq 37), a carbon-centered free radical is required for reduction.[187]

Table 8. MMA Chain-Transfer Constants[a] of Reaction 37 for Different Cobaloximes[296]

catalyst	substituents	axial ligands	K	E	(M^{-1} s^{-1})
6h	CH_3	CH_3	I	Py	120
6g	CH_3	CH_3	Cl	Py	200
6i	CH_3	CH_3	CNS	Py	200
6n		$-(CH_2)_4-$	Cl	Py	280
6p	Ph	Ph	Cl	H_2O	520
6q	Ph	Ph	Cl	Py	700
6r	Ph	Ph	Cl	$P(Ph)_3$	2800
6o	α-furyl	α-furyl	Cl	Py	1200
6m	CH_3	$COCH_3$	Cl	Py	800
6*l*	CH_3	$COOC_2H_5$	Cl	Py	1300

[a] Bulk MMA, 60 °C, [AIBN] = 0.04 M.

$$LCo^{III}-A + {}^{\bullet}R_n \rightarrow LCo^{II} + products \qquad (37)$$

The reduction can be effected by either MMA-propagating radicals or other tertiary radicals such as those provided by the decomposition of azo initiators. The reduction in eq 34 is autoaccelerated, indicating involvement of LCoH, most likely through eq 38.[304]

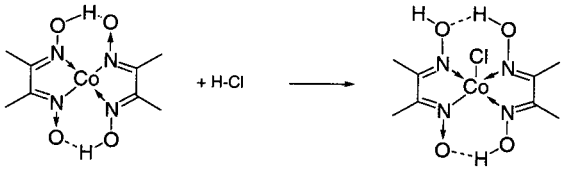
$$LCoH + LCo-A \rightarrow 2LCo + HA \qquad (38)$$

Unaccelerated rate constants of the reduction in eq 37 are several orders of magnitude less than k_{Co} (see Table 8).

The Co^{II} complexes obtained by eq 38 may interact with other products of the reaction such as HCl. While cobalt porphyrins are generally unaffected by counterions and byproducts, cobaloximes show complicated patterns of reactivity. When Co^{III}−Cl cobaloxime catalysts are re-isolated after catalysis, stoichiometric chloride is obtained despite the conclusion that the catalysts had passed through a Co^{II}, halide-free state. For Co^{III}−Cl cobaloxime catalysts, there is an induction period defined stoichiometrically

by when one free radical per one catalyst molecule has been consumed. After the induction period, k_{Co} was found to depend on the halide (as A ligand). Thus, cobaloxime **6g** (A = Cl) is 5 times more active than cobaloxime **6h** (A = I) in Table 1. Also, cobaloxime **6g** (A = Cl) is less active than the self-activating catalyst with A = sec-Bu (cobaloxime **6j**). These observations can be explained by invoking partial hydrolysis of the equatorial ligand through Scheme 6.

Scheme 6. Partial Hydrolysis of Cobaloxime



93

Addition of H^+ to any oxygen atom in the ligand interrupts the electronic ring current in cobaloxime, leading to lower effectiveness of the of newly formed cobalt chelate **93** to catalyze hydrogen transfer. A portion of the unreduced starting chelate can also be affected by the released hydrochloric acid to produce **94** and/or **95** (Scheme 7).

Addition of amides and alcohols at very low levels (3−5%) substantially increases the overall rate of reduction (eq 37).[296] This may be attributed to the formation of Co^{I} species, where LCo^{I} is the real reducing agent rather than LCoH in autocatalysis eq 38. The small amounts of amides and alcohols do not change the CCT chain-transfer constant after the induction period.

Cobaloximes are subject to poisoning by oxygen and peroxides much in the same manner as cobalt porphyrins. Low levels of benzoyl peroxide (BPO), cumyl hydroperoxide, or oxygen that are comparable with the concentration of the cobaloximes rapidly interfere with CCT. The degree of polymerization increases linearly with the BPO/LCo ratio but does not depend on the absolute concentration of either reagent over a wide range of concentrations (Figure 10).[296]

Kinetic analysis indicates that in the reaction of cobaloxime with BPO, the free radical forms by the mechanism of eq 36. The interaction of peroxides with cobalt species has been studied extensively.[296,305,306]

$$LCo^{II} + Bz_2O_2 \rightarrow LCo^{III} + BzO^{\bullet} \qquad (39)$$

The rate constant of oxidation eq 39 is 14 M^{-1} s^{-1}. Equation 39 leads to further radical consumption

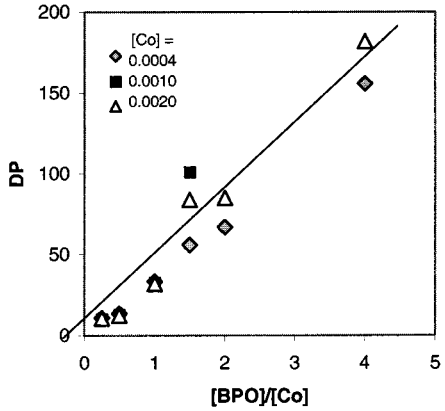


Figure 10. Dependence of the number-average degree of polymerization on the ratio of BPO to cobaloxime **6q**.[296]

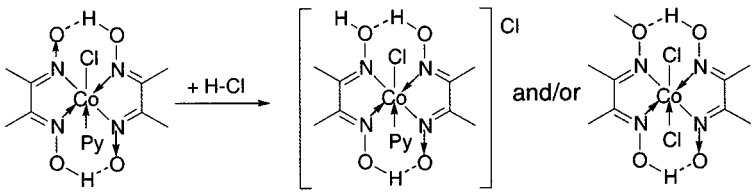
through Co^{III} reduction to Co^{II}, eq 37. The simultaneity of eqs 39 and 37 leads to a steady-state concentration of active Co^{II} species that provide MW control by CCT. Cumyl hydroperoxide behaves similarly to BPO in polymerization of methacrylates. Hence, in contrast to porphyrins, cobaloximes are poisoned reversibly by peroxides. In styrene polymerization, poisoning of the cobaloxime CCT agent is irreversible. Presumably, the presence of benzylic radicals during the BPO reaction leads to destruction of the equatorial ligand, through the possible intermediacy of Co^{IV} species.[307,308]

Acidic hydrolysis of CCT catalysts is described as a possible problem. Few actual measurements of the catalyst hydrolysis have been made. Addition of only 1% of acetic acid in MMA leads to a rate of cobaloxime deactivation of about 1.2% min^{-1} at 60 °C.[296] The stability of the BF_2-bridged cobaloxime is believed to be higher.[119,338,342] The complex $(dmgBF_2)_2$-Co^{II} decays at room temperature at a rate of about 0.6% min^{-1} at pH = 1 but is "practically stable" at neutral pH.[309,310] It should be noted, however, that these measurements were made in a benign solvent rather than in an active polymerization system involving free radicals.

Benzylcobaloximes decompose in strong acids, like 5% w/w sulfuric acid in water, at very low rates, ca. 0.002 mol/L min at 25 °C.[201] The secondary alkylcobaloxime, phenylethyl, is found to decompose only slightly faster under the same conditions, ca. 0.006 mol/L min. Although it is difficult to compare water and MMA solutions, the higher rate of cobaloxime decomposition in the presence of acetic acid is probably related to the instability of the hydrido cobaloxime and Co^{II} species versus the alkylcobaloxime.

Basic conditions not only convert CCT catalysts to CI catalysts (see section 3.6) but also promote cata-

Scheme 7. Halide Involvement in Cobaloxime Hydrolysis



94 **95**

lyst decomposition. Cobalt porphyrins and cobalt phthalocyanines are much more stable under basic pH and in the presence of free radicals than cobaloximes. Thus, the Co^{I} phthalocyanine that forms by reduction by free radicals in amides is very stable, being stored in a sealed glass ampule for 1 year without any change of its characteristic blue-green color. The more rapid decomposition of dioximates of Co^{I} is on a time frame comparable with polymerizations (0.06−2% min^{-1}).[188]

In conclusion, there are a variety of processes that can affect CCT by increasing or, more often, reducing the rate of the chain transfer by affecting the catalyst. Some of them are more pronounced at the beginning of polymerization, while others are become more significant at the end. The most common is the reversible or irreversible poisoning of CCT catalysts by peroxides because it is difficult to reduce the concentration of peroxides in the monomer to commonly used levels of catalyst (100 ppm or less). This is why erratic results on catalytic activity of cobalt chelates in CCT are not uncommon. Employment of low-conversion reactions (like 2−4%) makes testing results especially vulnerable. These side reaction can often be recognized by deviation from linearity of eq 1, but such careful investigation is not the norm.

4. Monomers for CCT

4.1. Methacrylates

Methacrylates are the monomers most commonly utilized in CCT, and MMA seems to be the monomer against which all comparisons are made. It was discussed extensively in the section on catalysts. In addition to the methyl ester, many other methacrylate esters are mention in the literature. Table 9 lists a variety of monomer for which chain-transfer constants are available or could be calculated. In keeping with patent strategies, many additional monomers are mentioned in patents but are not exemplified. Nonetheless, the monomers that have been studied[311] range from simple alkyl methacrylates to highly reactive species such as glycidyl methacrylates, 2-isocyanatoethyl methacrylates, or methacrylic acid[80] and to biologically derived materials such as 2-methacryloxyethyl phosphoryl choline, glycerol monomethyl methacrylate, or 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose.[312]

Table 9. CCT Chain-Transfer Constants[a] for Different Methacrylates[5,126,313−317]

ester group	C_C	catalyst	ref
$PhOC_2H_4-$	2000	**9c**	5
$(MeO)_3SiC_3H_6-$	27000 ± 1200	**9a**	313
$[Me_3SiO]_3SiC_3H_6-$	7500 ± 1400	**9a**	313
lauryl	20000 ± 1400	**9a**	313
3-(*N*-triazolyl)-4-hydroxyphenyl-	4000 ± 200	**9a**	313
$Me_2NC_2H_4-$	4400 ± 600	**9a**[b]	314
(*N*-phthalimidoyl)C_2H_4-	500	**9a**[c]	315
methyl	1300	**52**[d]	126
methyl	34000	**9c**	316
ethyl	26000	**9c**	316
butyl	16000	**9c**	316
methyl	2400	**1**	317
butyl	670	**1**	317
hexyl	430	**1**	317
heptyl	250	**1**	317
octyl	250	**1**	317
nonyl	150	**1**	317
decyl	110	**1**	317
hexadecyl	130	**1**	317
hydroxyethyl	1120	**9a**[e]	312
glycerol monomethyl	958	**9a**[e]	312
methacrylic acid	1058	**9a**[e]	312

[a] Polymerization conducted at 60 °C in neat monomer unless otherwise indicated. [b] 70 °C in neat monomer. Catalytic termination is observed. [c] Chain-transfer constant calculated on the basis of the article data. 80 °C; 30% in toluene. Catalytic termination is observed. [d] 50% monomer in supercritical CO_2. [e] In water.

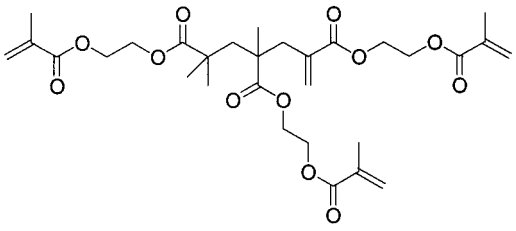
Several CCT catalysts are soluble in MMA but insoluble in the resulting polymer.[318] Interestingly, when these CCT catalysts are added to frontal polymerizations, they are carried in the polymerization front, decreasing the molecular weight throughout the resulting polymer.

In addition to standard methacrylates, it has been possible to extend CCT to carbohydrate-based systems.[319]

4.1.1. Di- and Trimethacrylates

Dimethacrylate monomers and polymethacrylate monomers must be discussed separately from other methacrylates because of their ability to cross-link under normal free-radical polymerization conditions. Even at very low conversion, less than 1%, they produce completely cross-linked polymers that cannot be solvent-swollen and are insoluble. CCT agents reduce molecular weight and thereby move the gelation point to a much higher degree of conversion, though CCT cannot prevent gelation completely.[320]

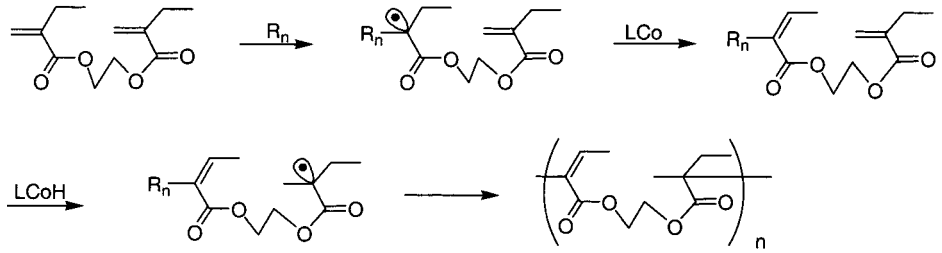
Hyperbranched polymers were synthesized by direct free-radical polymerization of ethylene glycol dimethacrylate monomer in the presence of a CCT catalyst. The free-radical homopolymerization of divinyl monomers is thought to selectively yield trimer **96**,[321,322] though previous work on oligomer distributions would indicate that this is unlikely.



96

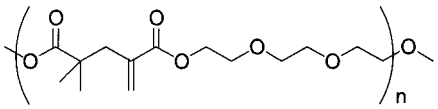
Polymerization of the trimers then leads to cascade branching, ultimately yielding soluble hyperbranched polymers instead of the insoluble networks obtained in the absence of the CCT catalyst. Terminating polymerization at moderate conversion provides highly reactive hyperbranched methacrylate. As mentioned above, there is some similarity between living radical polymerization and polymerizations carried out with high levels of CCT catalyst. Both processes preclude rapid chain growth by periodically interrupting chain growth. As a result, molecular weight tracks monomer conversion to a greater extent than it would in the absence of CCT. The oligomerization results in polymers with very low intrinsic viscosity.[323−325] The

Scheme 8. Oligomerization of Ethylene Glycol Diethacrylate



molecular weight and intrinsic viscosity of the hyperbranched polymers indicated that the average molecular weight ranged from a few thousand to more than 40 000. The reaction provides an alternative to the complex, multistep, routes to dendritic and starlike polymers. The superior physicochemical and molecular properties of star and dendrimer polymers[326] are believed to justify their very complex technology, but the cascading polymerization provides polymers that meet the requirements for many commercial applications where such perfection is not required.[36,327−329]

In a similar report utilizing triethylene glycol dimethacrylate, the polymer was described as a linear polyester.[330] Again, this description is probably incomplete, though it is possible at high catalyst loadings to prepare methacrylic dimers. Under ideal conditions, this would lead to the linear, unsaturated polymer **97**.



97

This was a single example with minimal characterization. A more direct approach to the polyester involves transesterification of the dimer with neopentyl glycol to oligomers and chain extension with diacids and glycols.[331] These species are effective pigment binders in paints.

Oligomerization of ethyleneglycol diethacrylate, EGEtA, provided polyester by radical polymerization according to Scheme 8.[332] Bis(dimethylglyoximato)-Co^{III}(benzil)(Py) as a CCT catalyst reduced the molecular weight of the resulting polymer. No rate constants were determined. The authors surprisingly observed that the yield of the oligomer increases with the concentration of the CCT catalyst. A similar dependence was found in AMS oligomerization and was attributed to minimization of bimolecular termination by rapid capture of the dimer radicals by CCT catalysts.[333] Related branched macromonomers were also prepared by copolymerization of methyl methacrylate with 1,6-hexanediol dimethacrylate in the presence of α-methylstyrene dimer as a molecular weight control (see section 5.1).[334]

Branched polymers can also be obtained by copolymerization of MMA with dimethacrylates based upon the condensation product of hexamethylenediisocyanate with two hydroxyethyl methacrylates.[335] This product is then further grafted with glycidyl methacrylate.

4.1.2. Emulsion Polymerization

The kinetics of solution polymerizations involving CCT are not substantially different from bulk polymerizations. An initial report that toluene as a solvent led to reduced catalysis rate[336] seems to be unfounded.[124]

Emulsion polymerization is an attractive route for making polymer compositions without solvent or with minimal amount of organic solvent.[32,94,337−340] CCT in emulsion polymerization may provide narrower polydispersity relative to noncatalytic chain-transfer agents.[339]

Starved-feed emulsion polymerization can be conducted without emulsifiers if suitable comonomers and procedures are utilized.[341] Polymerization of a water-soluble methacrylate like HEMA in the presence of a CCT agent is carried out initially. The resulting HEMA oligomer is further copolymerized with hydrophobic monomers so that the resulting diblock copolymer serves as a surfactant (see, for instance, sections 5.3 and 5.4). During the crosslinking process, all of this surfactant is incorporated into the polymer backbone and is thus immobilized, overcoming the problem of residual surfactant in the final product.

In contrast to solution polymerization, emulsion polymerization is more complex.[119] Monomer feeding can be crucial in obtaining the desired molecular weight.[342] The partitioning coefficient of the CCT agent between phases is another key factor.[343,344] The solubility of the cobaloxime catalysts can be regulated by the size of substituents on the equatorial ligand. The distribution coefficient for water/MMA drops sharply from 0.4 to 0.05 when the substituents in the equatorial ligand change from methyl to ethyl in **9**. Further increase of the substituent alkyl group does not change this ratio substantially.[120]

Generally, efficiency of CCT catalysis drops in emulsion polymerization. The following values of CCT chain-transfer constants may be compared with solution and bulk polymerization: $C_C^{MMA} = 1100\ M^{-1}\ s^{-1}$, $C_C^{EMA} = 640\ M^{-1}\ s^{-1}$, $C_C^{n-BMA} = 520\ M^{-1}\ s^{-1}$, $C_C^{2-EHMA} = 400\ M^{-1}\ s^{-1}$ (75 °C, water, **9a**).[342] In miniemulsion polymerization, the choice of catalyst depends on the choice of initiator (see Table 10).[345]

Azo initiators provide good catalyst activity in both solution and miniemulsion polymerizations, while the peroxide initiator $K_2S_2O_8$ substantially decreases the efficiency of molecular weight reduction by **9a**. The results in Table 10 may be explained by the ability

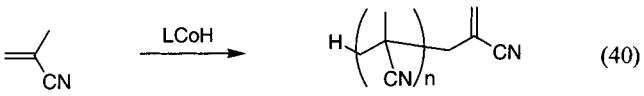
Table 10. Comparison of Miniemulsion (65 °C) and Bulk (60 °C) Polymerization[345]

		C_C	
initiator	catalyst	miniemulsion	bulk
AIBN	**9a**	21 000	24 000
AIBN	**9c**	11 000	14 000
$K_2S_2O_8$	**9**	830	
$K_2S_2O_8$	**9c**	12 000	

of potassium dipersulfate to oxidize the CCT catalyst when it is in the water phase. Since the **9c** catalyst is less soluble in water than **9a** catalyst, it is less susceptible to oxidation poisoning. In the case of **9c**, the peroxy radicals react with monomer rather than with the catalyst. More details on oxidative catalyst poisoning were given in section 3.7.

4.2. Methacrylonitrile

Methacrylonitrile is a slow polymerizing monomer under conditions of CCT, and it yields oligomer with a double-bond end group similar to methacrylates (eq 40). The resulting oligomeric products have a stronger tendency to copolymerize with additional monomer and thus be incorporated into subsequent polymer chains than do MMA oligomers.[139]



(40)

This tendency is presumably the result of the smaller size of the nitrile group relative to the ester group, so that reaction of LCoH with MAN oligomer is more competitive with that of the monomer. The chain-transfer constant C_C is not known for the polymeric MAN radical, but for the MAN dimer radical, the rate coefficient for CCT k_C is 8×10^5 M^{-1} s^{-1} (at 60 °C with $TAPCo^{II}$).[346]

4.3. α-Methyl Styrene

A major limitation of α-methylstyrene in free-radical polymerizations is its very low ceiling temperature of 61 °C.[347] As a result, AMS is utilized commercially only in radical copolymerization. Nonetheless, it is among the most active CCT monomers with $C_C = 9 \times 10^5$ at 50 °C for **9a** as CCT catalyst.[348] This value is relatively unchanged at 40 °C. This high value reflects the low $k_P = 1.7$ M^{-1} s^{-1} so that $k_C = 5 \times 10^5$ M^{-1} s^{-1}.

AMS dimer, AMSd (**98**), is useful as a radical addition−fragmentation−chain-transfer radical (RAFT) agent,[349−352] which is covered later. In the polymerization of styrene, AMSd is as active as methacrylate trimers and tetramers with a chain-transfer constant C_{AMSd} of 0.29 at 110 °C.[353] Although AMSd has been known to be a good molecular weight control agent for decades, commercially feasible methods for its manufacture have become available only recently. Most are based upon cationic polymerization. The major objective is to avoid internal Freidel−Crafts substitution to give the indane product a in Scheme 9. This reaction is the major reason cationic polymerization is not used for commercial polymerization of styrene or its derivatives.

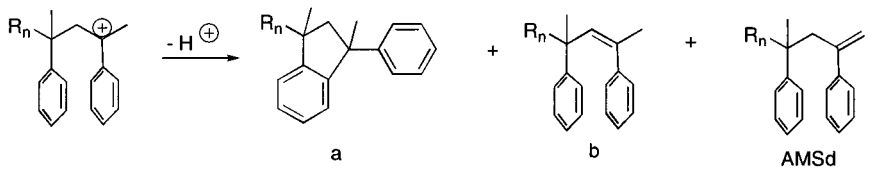
To minimize the indane, **99**, formation, dimerization was conducted in two-phase systems containing toluenesulfonic acid,[354] sulfuric acid,[355,356] electrophilic transition-metal complexes,[357] the polymeric solid-state acid Nafion,[358,359] metal oxide solid-state catalysts such as tungstophosphoric acid,[360] various zeolites,[361,362] mixed oxides,[363] and montmorillonite clay in the presence of organic solvents.[364,365] The major limitation of the cationic approach, however, is the unavoidable formation of internal isomer **100**. Since isomer **100** is inert in radical polymerization, the lower the content of isomer **100**, the higher activity of the **98** mixture. Even in the very best cases, its presence is never less than 5−15%.

CCT also can be employed to synthesize **98**.[366] Temperatures over 150 °C facilitate the process. A process yielding undetectable levels (probably, <0.2%) of isomer **99** in the final AMSd, **98**, provides a high-quality process for AMS dimerization.[367] Apparently, the "ceiling temperature" of the dimer of AMS is much higher than that of AMS polymer. The monomeric radical obtained in reaction with LCoH is capable of adding one or two monomeric units but then sterics reduce the value of the propagation rate constant, thereby preventing further radical growth. The decrease in propagation rate constant improves the efficiency of any chain-terminating reactions. As emphasized earlier,[61] low MW polymer chemistry is significantly different from that of high polymer. Many concepts and equations well established for conventional polymer science may encounter serious limitations when used to describe oligomers with DP < 6.

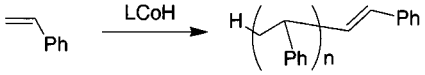
4.4. Styrene

While there is a considerable body of research on CCT polymerizations of styrene itself, there are no reports of CCT in polymerizations of substituted styrenes. In the case of styrene as well as in the case of other vinylic monomers bearing no methyl group adjacent to the propagating radical, CCT always provides oligomers with an exclusively trans configuration of the double bond.[28,368] Because there is no abstractable methyl hydrogen atom, the only site for

Scheme 9. Cationic Oligomerization of α-Methylstyrene



hydrogen atom abstraction is the methylene group (eq 41). In proton NMR spectra, the vinylic protons of the styrene end group appear as a singlet due to a strong AB-type interaction. However, this singlet can be observed as two peaks at 6.40 and 6.43 ppm by high-field NMR.



(41)

The chain-transfer constants for styrene polymerization with porphyrinic CCT catalysts are given in Table 4. In addition, the following values can be found in the literature: $k_C = 1.4 \times 10^5$ M^{-1} s^{-1} (40−70 °C, **9a**),[314] and $k_{C_C} = 6.4 \times 10^4$ M^{-1} s^{-1}, $C_S = 400$ (40 °C, **9c**).[40] The low C_S in styrene systems can be partly attributed to the formation of Co−C bonds, reducing the concentration of active Co^{II} catalyst. The experimental observation that the molecular weight distribution of the polymer formed in CCT remains constant with conversion is not explained.[369]

Styrene is capable of forming moderately stable Co-C bonds.[370] The formation and decomposition of adducts between the CCT catalysts and the propagating radicals results in "reversible inhibition".[123,271] In this case, an induction period is observed at the beginning of polymerization. This induction period is characterized by the steady growth of the rate of polymerization similar to the classic kinetics of a polymerization inhibited by a weak inhibitor. Depending upon conditions, the time required to reach steady-state polymerization kinetics (eq 42) may require tens of minutes.

$$LCo + R_n \rightleftharpoons LCo{-}R_n \qquad (42)$$

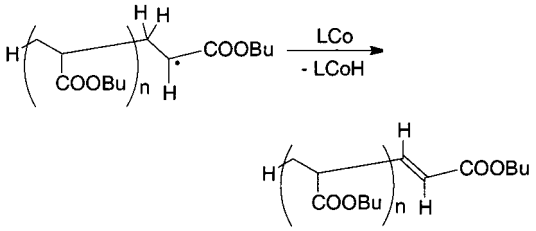
This period of time may be comparable with the experimental frequency of sampling the reaction mixture, thereby confusing the reduction of molecular weight attributable to formation and dissociation of the corresponding organometallic species with the reduction of molecular weight due to CCT.[371] Moreover, continuous decomposition of the CCT catalyst during polymerization has been observed.[372] As a result, some values of the apparent chain-transfer constants of CCT for styrene and other vinylic monomers would be time dependent. Molecular weight distributions at moderate and high conversions can be bimodal.[123] These styrene polymerizations are in contrast to MMA polymerization at high conversion that follow kinetic model predictions with only a slight accumulation of lower MW products due to reduction of monomer concentration toward the end of polymerization.[118] Consistent with the formation of an equilibrium concentration of Co^{III}−alkyl, C_C was found to be less that 100 in the dark but increases to a maximum value of 5000 under UV irradiation. Previous work has demonstrated the photolysis of the Co−R bond.[285−288] The value of C_C was also found to be dependent upon the initiator concentration, decreasing with higher initiator levels.[125] Both of these observations are consistent with the formation of a large equilibrium concentration of Co^{III}−R that can be converted back to Co^{II} photochemically.

4.5. Acrylates

Catalytic chain transfer in acrylate polymerizations is problematic due to the propensity of acrylates to form stable Co−C bonds between the CCT agent and the propagating radical of both the monomer and its oligomers.[268,269,373] It has even been possible to observe a growing polymer chain terminated with a Co−C bond directly by MALDI.[374] This bond is stronger than that in the case of styrene. These complications have a direct impact on the use of CCT in acrylic polymerizations.

Starting with a Co^{II} CCT catalyst, the initial radicals formed will react with the Co^{II} forming Co^{III}−R, thereby effectively removing much of the Co^{II} from the reaction mixture. This reaction was originally described as "reversible inhibition".[375] This has the effect of trapping all of the initiating radicals and causing an induction period in the polymerization until the Co^{II} is essentially consumed. Once a stoichiometric number of initiating radicals have been produced, polymerization starts but the product is relatively high in molecular weight. The catalyst appears to be relatively ineffective because the concentration of Co^{II} is low. Nonetheless, there is a finite equilibrium concentration of Co^{II} that is low relative to the quantity of catalyst charged but still high relative to the concentration of propagating radicals. There is also a slow reversible reaction of Co^{III}−R liberating radicals to reinitiate polymerization.[376−378] Similar phenomena have been observed with other reversible capping agents for the propagating radical chains.[379,380] The suggestion to change the term "reversible inhibition" to "deactivation"[381] is not an improvement because in addition to reversible inhibition there are other reactions that can deactivate capping agents in living radical polymerizations.

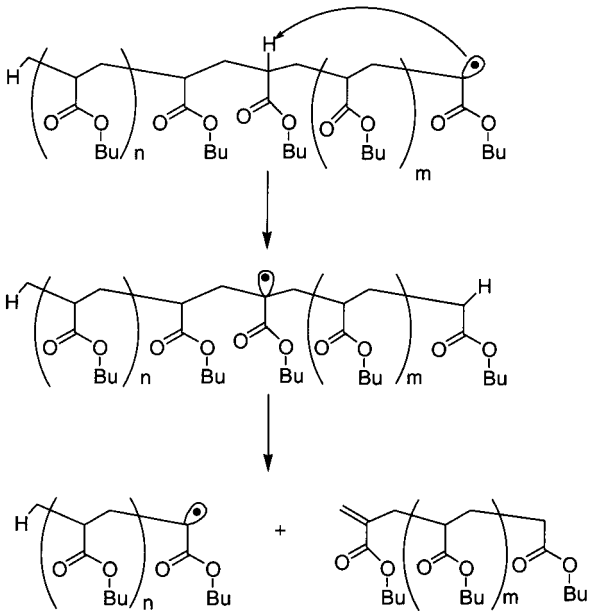
The accepted approach to overcoming this limitation is to increase the temperature of the process.[382,383] This observation is additional evidence that the intermediate state in CCT, hydrogen atom abstraction from the propagating radical (eq 43), involves a caged radical pair rather than an adduct of the propagating radical with the cobalt chelate.



(43)

A characteristic feature of acrylate polymerization is the reaction of "radical back-biting".[384−387] Due to the high activity of the acrylic propagating radical and the presence of substantial numbers of tertiary hydrogen atoms in the polyacrylate backbone, a propagating radical can abstract a hydrogen atom from itself or from another polyacrylate molecule. According to the proposed mechanism shown in Scheme 10, the newly formed radical may undergo

Scheme 10. Back-Biting in Growing Acrylate Chains

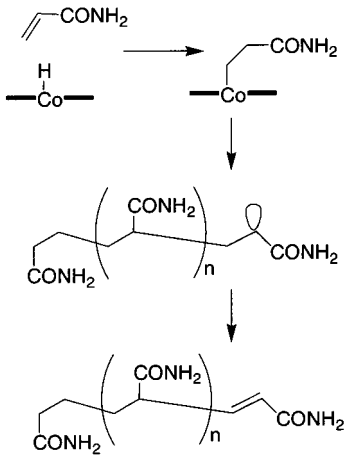


fragmentation. The net result of the back-biting is the formation of oligomer with a terminal double bond of a "methacrylate moiety" with vinylic proton resonances at 6.2 and 5.5 ppm.[383] When the polymerization of acrylic acid is conducted at temperatures above 225 °C, the resulting oligomers have a DP below 50.[388] The products are useful as detergent additives and for subsequent polymerization.

Originally the reaction in Scheme 10 was discovered at temperatures approaching 240 °C,[388] which are close to the ceiling temperature of acrylates. More recently it was demonstrated that this process is relatively independent of temperature and can be observed as low as 90 °C. Thus, the polymerization of acrylates in the presence of CCT may result in a mixture of vinyl-terminated products.

Another "side reaction" in the polymerization of acrylates could be the anti-Markovnikov addition of Co−H to the olefinic double bond. This reaction shown in Scheme 11 was suggested to explain the absence of any methyl group in the polymer backbone of acrylamide radically polymerized in the presence

Scheme 11. Proposed Mechanism to Explain Poly(acrylamide) Structure

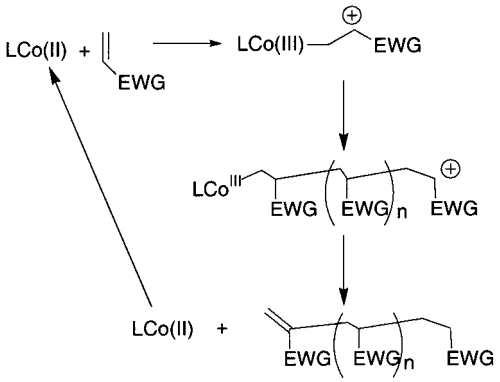


of a CCT catalyst.[389] The Markovnikov hydrogen atom addition normally observed in CCT requires that one methyl group should start each polymer molecule and each should be terminated by one vinylic end. In the case of acrylamide, the theoretical number of vinylic hydrogen atoms was observed but expected resonances attributable to CH_3-CH at the head of the chain were absent.

It cannot be excluded that the back-biting depicted in Scheme 10 could be responsible for the observed absence of methyl proton.[389] Scheme 10 would leave most of the dead polymer molecules without methyl end groups. The chemical shifts of the vinylic protons in the resulting oligo-acrylamides are at 5.75 and 6.25 ppm, which is similar to the methacrylate end group of polyBA which has been terminated by back-biting. In oligo-acrylates produced by CCT, the vinylic protons have resonances at 6.8 and 5.85 ppm.[383] The mechanism of Scheme 11 in acrylate polymerization requires additional study.

There is a cationic analogue of Scheme 11 when *N*-vinyl carbazole polymerization was induced by poly(vinyl chloride)-bound dimethylglyoxime complexes of Co^{II}, Ni^{II}, and even Cu^{II} (Scheme 12).[390]

Scheme 12. Cationic Route to Macromonomers



The polymerization shown in Scheme 12 was observed at room temperature and explains the stoichiometric formation of vinylidene end groups. This reaction seems to be a cationic polymerization rather than an example of CCT.

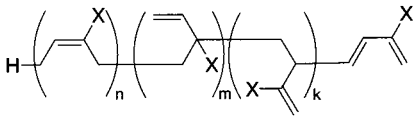
Finally, Scheme 10 is a good example that interesting chemistry remains to be found even in well-studied polymerization systems. In addition to acrylates, substantial back-biting occurs even in radically polymerized styrene.[383] Despite the long-standing utilization of acrylates in radical polymerization, the reaction shown in Scheme 10 was overlooked.

4.6. Acrylonitrile

Investigation of CCT homopolymerization of acrylonitrile is difficult as a result of the insolubility of polyAN even at low molecular weight. Copolymerization with styrene was reported.[297,371] Addition of minor quantities of amines (about 3%) was shown to have a positive synergetic effect on CCT at 60 °C (bis-(diphenylglyoximatoCo^{II}(Py)Cl, AIBN). The role of amines is possibly to labilize the Co−C bond with formation of a π-complex instead.

4.7. Dienes

Polymerizations involving CCT of this interesting class of monomers has been described in only one reference.[391] The polymerization of dienes in the presence of CCT catalysts provides oligomers, **101**, with a terminal pair of conjugated double bonds, **101d**.



101-a b c d

Diene monomers can be considered to be difunctional monomers. In addition to "normal" 1,4-polymerization that produces polymer with 2,3-vinyledene double bonds **101a**, 1,2-polymerization leads to pendant vinyl groups **101b** and **101c** as well.[392] (For simplicity, not all possible isomers are being considered.) These pendant vinyl groups are able to propagate in further radical polymerization, thereby complicating the polymerization, but they also provide functionality for further chemical cross-linking in the final product. In this respect polymerization of diene monomers is somewhat similar to polymerization of dimethacrylates described above, but there are two important differences. First, the groups **101c** and especially **101b** are much less reactive in radical polymerization than the double bonds in methacrylates. Second, the number of pendant vinyl groups **101b** and **101c** per chain in polydienes is substantially less than the number of pendant groups in dimethacrylates. In polychloroprene, for example, the combined vinyl groups account for about 10% of all double bonds.[393]

CCT suppresses the gel effect in radical polymerization of chloroprene. The polydispersity stays low, <2, up to 80% conversion. Then, because of cross-linking through pendant vinyl group, both the polydispersity and the molecular weight start to grow exponentially. Table 11 summarizes the use of CCT in polymerization of several commercially significant dienes.

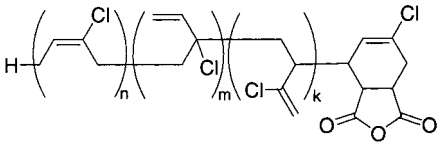
Table 11. CCT in Radical Polymerization of Different Diene Monomers[391]

	isoprene	chloroprene	2,3-dichlorobutadiene
C_C[a]	190	30	<14
k_C ($M^{-1}s^{-1}$)	75 000	50 000	N/A
k_P ($M^{-1}s^{-1}$)	~400[b]	1700[c]	N/A

[a] Solution polymerization of 67% v/v diene in 1,2-dichloroethane, 70 °C, $(dmgBF_2)_2Co^{II}(MeOH)_2$, [AIBN] = 8 g/L, 30% conversion. [b] Estimate from ref 394. [c] From ref 395.

The presence of electron-withdrawing substituents such as halogen on dienes substantially increases their propagation rate constants and reduces termination rate constants. As shown in Table 11, k_{Co} does not increase from isoprene to chloroprene so that C_C decreases. The trend continues for 2,3-dichlorodutadiene. Although the propagation rate constant for 1,2-dichlorobutadiene is not known, its C_C is less than that of chloroprene by a factor of 2 or more, which could be attributed to higher steric constraint around the radical center created by the two chlorine substituents. The paucity of information on propagation rate constants of diene monomers in free-radical polymerization limits further physical studies in this area. The only other reported value of k_P for isoprene is 2 orders of magnitude smaller.[396]

The reactivity of conjugated double bonds is significantly different from that of isolated double bonds in the polymer backbone of polydienes. This difference can be used for selective chemical modification of the dienes with reactions such as the Diels–Alder reaction. With maleic anhydride as an enophile, selective addition to the terminal pair of conjugated double bonds in a chloroprene oligomer is complete in a few hours to give **102**.[391]

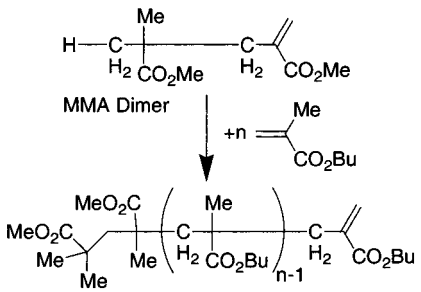


102

According to MALDI-TOF, only one MAn molecule per one chloroprene oligomer is added.

4.8. Macromonomer Reinitiation and Nonpolymerizable Monomers

It had been demonstrated that MMA macromonomers do not copolymerize with methacrylates under normal polymerization conditions, and it had also been stated that they do not copolymerize under CCT conditions.[110] While this is true, experiments involving cobalt-catalyzed deuterium exchange between MMA dimer and MMA-d_8 made it clear that the Co–H or Co–D was adding to the double bond of the dimer to give radical, suggesting that the dimer was being converted to dimer radical. Distilled MMA dimer was exposed to butyl methacrylate under normal CCT polymerization conditions. It was observed that in addition to the expected BMA oligomers and starting MMA dimer, there were species involving MMA dimer coupled with BMA as in eq 44.[397,398]

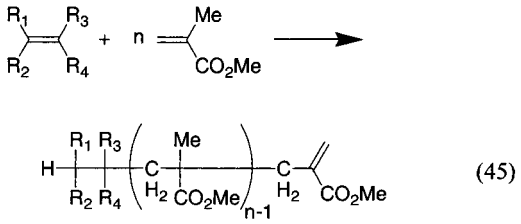


(44)

It was already known that MMA dimer was not incorporated into BMA polymer under normal free-radical conditions, though it would act as a chain-transfer agent (see RAFT, section 5.3). It is thus possible to reinitiate seemingly dead polymer chains by addition of a hydrogen atom.

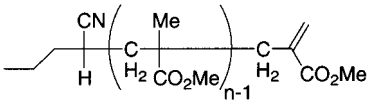
This reinitiation is of commercial interest in a number of circumstances. In preparation of low oligomers by CCT, large quantities of dimer are formed, but dimer is often less attractive than the other oligomers for reasons of activity and volatility. Dimer could be distilled out of the higher oligomers and combined with additional monomer in the oligomerization process to be converted to higher molecular weight species. An extruder-based process for synthesis of lower macromonomers would involve recycle of monomer.[107] In addition, it is possible to react the dimers or oligomers of one monomer with a second monomer, thereby forming block copolymers. The resulting polymers would be a complex mixture with homopolymer of the new monomers, but there are some applications where this would not be a complication.

Extension of macromonomer reinitiation led to copolymerizations with "nonpolymerizable monomers".[399−401] Methacrylate oligomers cannot be homopolymerized due to the steric bulk of the substituents at what would be the radical center. Thus, they are subject only to reinitiation under CCT conditions. There are many other olefinically unsaturated species which do not undergo homopolymerization or copolymerization with normal free-radical monomers.[402] These can by represented by the tetrasubstituted olefin in eq 45, though more often the desired olefin is 1,2-disubstituted.

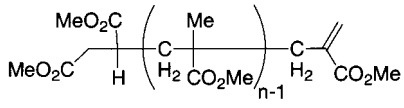


(45)

For instance, 2-pentenenitrile with MMA gave **103** and dimethyl maleate gave **104**, but both contained MMA homooligomers.



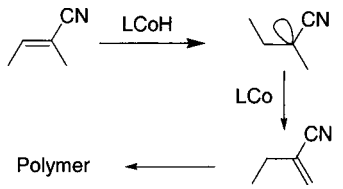
103



104

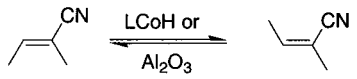
Other examples of nonpolymerizable monomers included 2-cyano-2-butene, crotonaldehyde, ethyl crotonate, and cyclopentene-1-one. The reactions are most productive if carried out with very high concentrations of the nonpolymerizable monomer relative to the conventional monomer. Where possible, the nonpolymerizable monomer is the solvent for the reaction and the conventional monomer would be added under starved-feed conditions. Such an approach would minimize the percentage of chains initiated with the conventional monomer.

An attempt to polymerize 2-methyl-2-butenenitrile, MBN, by first isomerizing to methylenebuteronitrile (eq 46) led to isomerization instead (eq 47).



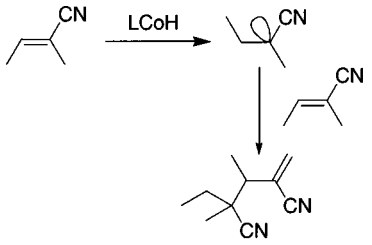
(46)

Heating an $E/Z = 1{:}2$ mixture of MBN isomers in the presence of AIBN and a cobalt catalyst results in the reverse composition of *E* and *Z* isomers, 2:1, in 2 h.



(47)

Without cobalt chelate and azo initiator there was no change. Oligomerization (eq 48) also occurs, but the rate is several orders of magnitude slower.



(48)

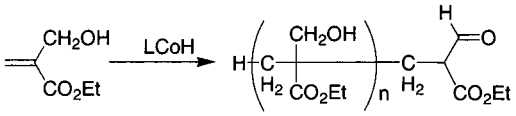
For reasons not understood, heating the isomer mixture with basic alumina causes the reverse transformation, restoring the original 1:2 ratio between MBN isomers. Formation of radical species from MBN was confirmed by observation of copolymer with MMA when minor quantities of MMA were added into a reaction mixture of MBN, cobalt porphyrin, and AIBN.[139] Therefore, we may draw the conclusion that H-abstraction from the methyl group from the propagating radical of methacrylates is governed by bulk substituents in the propagating radical and the large planar structure of CCT catalyst.

4.9. Isomerizational CCT

Vitamin B_{12} is known for its ability to catalyze molecular rearrangements. A variety of cobalt chelates are logical models for vitamin B_{12}, and their stoichiometric and catalytic activities in a variety of reactions,[403] particularly olefin isomerizations, were studied intensively.[404−411] Noncatalytic isomerization reactions based upon the synthesis of alkylcobalt chelates as model intermediates were favored. A variety of catalytic oxidations of substrates such as hydroquinone, azo compounds, phosphines, and olefins were also investigated.[412−415] Copolymerization of α-methylstyrene and other monomers with oxygen in the presence of CoTPP led to alternating polyperoxides.[416−418] Cobaloximes were found to catalyze

the alkylation of alkenes and aldehydes by organozinc compounds.[419,420] Catalytic hydrogenation of olefinic double bonds is a well-known reaction.[180,421−423] It is therefore interesting that within the limits of detection (<1%), hydrogenation of double bonds was never observed in CCT.

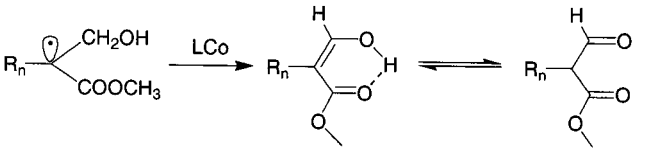
Polymerization of monomers containing α-hydroxymethyl groups results in oligomers terminated with an aldehyde group.[424−427] For instance, eq 49 shows the reaction for conversion of ethyl α-hydroxymethylacrylate, EHMA, to **105**.



(49)

105

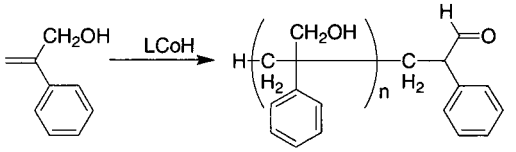
Apparently, the cobalt catalyst abstracts a hydrogen atom from the α-methylene group. The resulting enol is stabilized by isomerization to an aldehyde and formation of a quasi-aromatic ring through a hydrogen bond (eq 50).



(50)

The ratio between enol and aldehyde isomers is about 1.4. The chain-transfer constant in eq 49 (C_C = 700) is an order of magnitude less than that of MMA. One may conclude that this value reflects steric obstruction of the methylene group by the OH group and that there is no significant enthalpy gain in the enol structure shown in eq 50 relative to a PMMA terminal double bond.

The reaction is even more efficient for 2-phenylallyl alcohol (eq 51) and particularly its copolymers, yielding the oligomer with a terminal aldehyde, **106**.



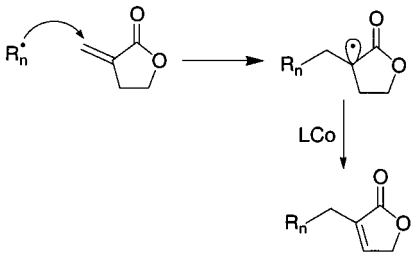
(51)

106

To ensure uniform end-group functionality, careful selection of the comonomers is necessary, but the approach is described.

Attempts to use other hydroxymethyl monomers such as allyl alcohol, 2-methylallyl alcohol, and 2-chloroallyl alcohol for isomerizational copolymerizations with methyl acrylate gave mixed results due to the poor copolymerization rate constants of these olefins and the ability of acrylic radicals to abstract hydrogen atoms from allyl alcohols.

Another example of iCCT comes from polymerization of α-methylenebutyrolactone (MBL).[428] CCT from the radical derived from this monomer leads to the unsaturated lactone shown in eq 52.



(52)

Usually, monomers without methyl groups in the position α to the double bond are several times less active that those with an α-methyl group. For instance, the polymerization of EHMA above is a good example. MBL was expected to be active in CCT, but the activity observed was unexpected. Its C_C was 8 × 10^4, while C_C for MMA is 4 × 10^4. The keto−enol tautomerization (eq 53) is responsible for the high CCT rates because the product of the tautomerism is further stabilized by aromaticity.

(53)

107 **108**

Such tautomerism is not possible in MBL monomer but becomes possible after hydrogen atom abstraction by CCT. The enol form (**108**) of the lactone (**108**) is a substituted hydroxyfuran.

Isomerizational CCT is an additional tool to produce end groups with chemical functionality different from that of normal CCT. Both EHMA and MBL provide end groups that are quite reactive toward electrophiles. For successful application in iCCT, the monomers should allow a significant thermodynamic driving force by addition of a free radical followed by hydrogen atom abstraction and isomerization.

4.10. Copolymerizations

A combination of variables controls the outcome of the copolymerization of two or more unsaturated monomers by CCT free-radical polymerization.[382] Of course, all of the features that control the outcome of a normal free-radical polymerization come into effect.[40,426,429] These include the molar ratio of monomers, their relative reactivity ratios and their normal chain-transfer constants, the polymerization temperature, and the conversion. In the presence of a CCT catalyst, the important variables also include their relative CCT chain-transfer constants and the concentration of the Co chain-transfer agent. The combination of all of these features controls the molecular weight of the polymer and the nature of the vinyl end group. In addition, they can also control the degree of branching of the product.

In a typical copolymerization involving monomers that are considered to be good for CCT[311] in combination with those that are less effective,[430] it is typical that the chain-transfer constant of a given catalyst diminishes.[135] It is also observed that there is a period of inhibition of polymerization which is dependent upon the concentration of catalyst and the ratio and

Table 12. Copolymerization Chain-Transfer Constants, C_C, for Selected Catalysts

composition			catalyst		
MMA	BA	St	**39b**	**39c**	**5s**
10	0	0	1200	3500	630
9	1	0	1000	560	184
8	1	1	700	500	200
5	5	0	440	130	31

Calculated from ref 135.

nature of monomers.[431] The catalysts in Table 12 were prepared in situ rather than under optimized conditions, making the results a questionable combination of solubilities, formation rate constants, and chain-transfer constants. Nonetheless, the effects in copolymerizations presented in Table 12 are typical. Addition of butyl acrylate or styrene lowers the effective C_C, and the reduction can be significant.

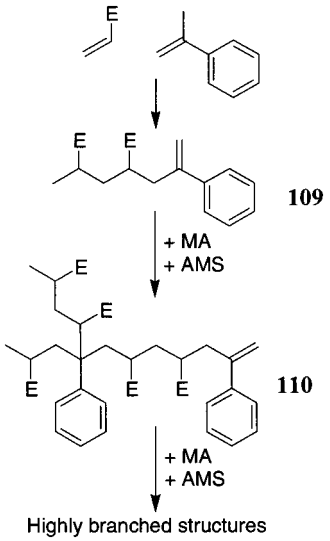
In a copolymerization of styrene and methyl methacrylate under CCT conditions, the fraction of unsaturated styrene end groups is proportional to the fraction of styrene in the monomer feed.[368] Due to the stability of styrene radicals, the relative fraction of propagating styrene radicals is large over the whole range of monomer feed compositions.[432,433] This feature complicates the determination of radical reactivity ratios but may be compensated for by measuring the average transfer rate coefficient as a function of monomer feed composition.

Measurement of reactivity ratios under normal free-radical and CCT polymerization conditions indicates that CCT is a modified free-radical polymerization as expected.[434] The reactivity ratios for MMA and butyl methacrylate were used as a mechanistic probe. Reactivity ratios were 1.04 and 0.81 for classical anionic polymerization, 1.10 and 0.72 for alkyllithium/trialkylaluminum initiated polymerization, 1.76 and 0.67 for group transfer polymerization, 0.98 and 1.26 for atom transfer radical polymerization, 0.75 and 0.98 for CCT, and 0.93 and 1.22 for classical free-radical polymerization. These ratios suggest that ATRP and CCT proceed via radical propagation.

The composition of CCT copolymerization products has been explored in a more complete manner utilizing matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.[435] The bivariate distributions of monomer composition and chain length were determined for a series of copolymers of MMA and butyl methacrylate (BMA) produced by CCT. The relationship between the distributions of copolymers and the kinetics of the copolymerization reactions was derived using the terminal copolymerization model.[436,437] The reactivity ratios, CCT coefficients, and initiator selectivities were $r^{MMA} = 1.09$ and $r^{BMA} = 0.77$, $C_C^{MMA} = 17\,900$ and $C_C^{BMA} = 6150$, and $S^{MMA} = 0.535$, respectively. The reactivity ratios for these polymerizations by ^{1}H NMR ($r^{MMA} = 0.75$ and $r^{BMA} = 0.98$) were in general agreement.

Monomers that form tertiary radicals bearing methyl substituents are generally considered to be good CCT monomers. These include MMA, AMS, and methacrylonitrile.[311] In addition, dienes can be good CCT monomers. Monomers that form secondary radicals or do not possess methyl substituents are generally considered to be poor CCT monomers.[430] These include MA, styrene, acrylonitrile, and vinyl acetate. Copolymerization of the good CCT monomers with poor CCT monomers in the presence of a CCT catalyst leads initially to oligomers terminated after the incorporation of a good CCT monomer. Thus, in general, the mixed oligomers will contain a terminal methylene unit. For example, copolymerization of methyl acrylate with α-methylstyrene mixture in the presence of a CCT catalyst leads initially to oligomers with a terminal double bond.[374] As shown in Scheme 13, the most frequent product will be oligomers of

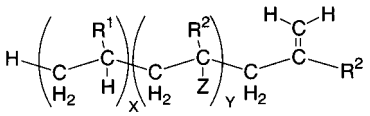
Scheme 13. Illustrative Products in Methyl Acrylate Copolymerization with α-Methylstyrene: E = CO_2Me



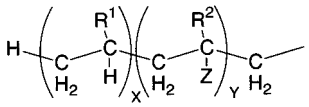
methyl acrylate terminated with an α-methylstyrene moiety, **109**. The methyl acrylate radical is highly reactive but spends much of its time coordinated to the cobalt catalyst.

Insertion of a single AMS leads to a relatively stable radical with an appreciable lifetime. Because AMS is an effective CCT monomer, generating a growing radical with an available methyl C−H bond, CCT occurs with high probability, producing structure **109** that has a terminal double bond that is reactive toward poor CCT monomers. The unsaturated species, **109**, is a copolymerizable monomer that can be incorporated into an additional growing polymer chain forming a branch point. Incorporation of **109** again leads to a relatively stable radical species, but unlike AMS incorporation, it does not provide a readily accessible methyl at the radical center, so continued propagation is the most likely outcome. Early in the polymerization this is an unlikely event, but as the other monomers are depleted, the relative molar concentration of **109** increases, leading ultimately to a substantial portion of branched product, **110**. At high conversion, the concentrations of AMS, MA, **109**, and **110** become similar and a complicated dendritic structure emerges. The ultimate product has been described by structure **111**, where the R^1 and R^2 substituents are typically

carboalkoxy, phenyl, or cyano and where Z is typically methyl.



111



112

In addition, Z can be described by **112**. When Z is methyl, structure **111** would be a simple random copolymer of the poor monomer bearing only R^1, terminated by the good comonomer bearing a methyl and R^2. Interestingly, Z can be a single branch **112** when it contains only methyl as Z, but **112** can also contain additional branches again defined by **112**, building into a highly branched system.

The entire process relies upon elevated temperatures to destabilize any Co^{III}−alkyls and high catalyst concentrations such that ample Co^{II} is available. This also leads to relatively low molecular weights for the initial products. It also helps that the susceptibilities of the two monomers to CCT are significantly different and that the concentration of the good CCT monomer is high. Unbranched structures are favored by low conversion, while high conversion favors reinsertion and high branching. The low molecular weight and resulting higher concentration of oligomers favors reincorporation and branching.

Scheme 13 may be generalized by describing A-type monomers[311] and B-type monomers.[430] A-type monomers provide chain termination and branching. The A monomers would stay mostly in the branching point. Because B-type monomers are not nearly as effective for CCT, they are generally not the ultimate group in resulting macromonomers. Nonetheless, they are capable of copolymerizing both with the A monomers and with the olefinically terminated macromonomers. Thus, they incorporate oligomers and monomers into higher polymer. In Scheme 13 one can understand how the structure of the final product depends on the relative concentration of oligomers, A monomers, B monomers, and cobalt catalyst. In Table 13, the results of butyl acrylate copolymerization with 20% MMA are presented.

Table 13. Batch Polymerization of BA:MMA (4 v/v mixture at 90 °C)[a]

time (h)	1.5	3	7	22
percent conversion	12	24	55	93
M_n	540	640	890	2300
PDI	2.08	2.08	7	2.8

[a] A 50% solution in 1,2-dichloroethane, [VAZO-88] = 2 g/L; [cobaloxime 8] = 0.25 g/L.

Because MMA is incorporated into polymer chains more rapidly, the concentration of MMA decreases steadily relative to BA during the course of the polymerization while the concentration of terminally unsaturated macromonomers is steadily increasing. These varying concentrations favor the formation of highly branched polymer at high conversion.

The product may be of more complex structure if more than two monomers are utilized. For example, if nonhomopolymerizable monomers as described above[402] are included at the beginning of the polymerization, the final product would have them on the periphery of the branched structure. Feeding the polymerization with different monomers would provide additional flexibility to this "arms-first" approach of making hyperbranched polymers.

Batch polymerizations of styrene, MMA, and 2-hydroxyethyl methacrylate carried out in the presence of either dodecanethiol or **9c** indicate that the overall rates of polymerization do not differ significantly in the two systems.[438] The molecular weight distribution of the polymer formed in the presence of the thiol becomes increasingly broad, whereas the **9c**-mediated polymerization produces a relatively uniform product during the course of the reaction. The polymer product formed with **9c** was found to be slightly less stable thermally than the product formed by the thiol, presumably a result of the unsaturated end groups.

To prepare water-soluble polymers employing CCT, it is necessary to modify the polymerization conditions.[312,439] Use of a standard batch reaction leads to hydrolysis of catalyst, changing the catalyst level over the course of the polymerization, yielding a mixture of products and poor control of the reaction. A feed or starved-feed process that adds catalyst over the course of the reaction maintains a constant catalyst level and high conversion. The approach can be applied to a range of monomers such as methacrylic acid, 2-aminoethyl methacrylate hydrochloride, 2-hydroxyethyl methacrylate, 2-methacryloxyethyl phosphoryl choline, glycerol monomethyl methacrylate, and 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose.

5. Applications of CCT Products

In general, the products of CCT are utilized in further chemistry, but there are some applications where they are employed directly. For instance, CCT catalysts may be used directly in the preparation of emulsions for electrophotographic toners.[340] The resulting emulsions are more stable than those obtained with thiol chain-transfer reagents. They may be combined directly with suspensions of black or colored pigments and precipitated to yield toners of narrow particle size. Apparently there may be occasions where highly bimodal molecular weight distributions are desired for toner applications, and then the CCT catalyst is added partway through the polymerization.[440,441] Alternatively, the CCT catalysts may be employed directly in the casting composition for thermoformable sheet compositions, lowering viscosities and improving toughness of the final sheet goods.[442]

For some application sensitive to color, it may be necessary to decolorize some macromonomers. The process used is dependent on the properties of the

macromonomer and the catalyst used in its preparation.[443,444] While most polymerizations are carried out in batch reactions or starved-feed reactions, continuous reactors can also be employed.[445]

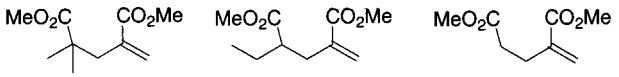
Ethylene−vinyl alcohol copolymers are important oxygen barrier resins for the food packaging industry, and aesthetics of the packaging films are important. The role of α-methylstyrene dimer added to ethylene−vinyl acetate copolymers after polymerization but before saponification is difficult to understand. Nonetheless, the resulting polymers have the advantages of good melt extrusion stability and drawdown resistance resulting in films without streaking.[446] In addition, they have good interlayer adhesiveness and gas barrier properties.

5.1. Reduction of MW

Federal requirements to produce increasingly lower VOC paints[34] have been a significant driver of CCT technology.[447] Telechelic polymers and other functional systems are used as low-viscosity reactive cross-linkers,[35] and pigment dispersants.[37]

A good example of cross-linking utilizing low molecular weight oligomers involves poly(ortho esters) and isocyanates.[448] Oligomers of hydroxyethyl methacrylate provide multiple hydroxyl groups for reaction of trimethyl orthoformate and hexamethylene diisocyanate trimer, in the presence of a sulfonate catalyst, to give a product with flowability for application but which cures to give good weatherability and adhesion. Similar systems are useful for the electrodeposited underlayer used for corrosion resistance in automotive finishes.[449]

The MMA dimer, **113**, readily prepared by CCT, is not homopolymerizable; this is attributed to the steric constraints imposed by the steric bulk appended to the α-position.[450] Interestingly, the isomeric olefin **114** can be polymerized to low molecular weight,[451] and the less hindered species **115** is readily polymerized to higher molecular weight,[452] though in both cases fragmentation chain transfer is observed. In copolymerization with MMA, **114** acts as a chain-transfer agent.

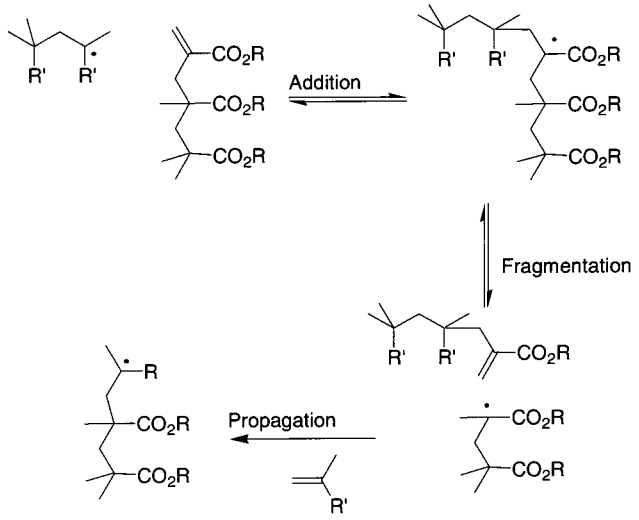


113 **114** **115**

All three species are copolymerizable with styrene. The three species were prepared in interesting solid-state dimerizations involving their salts and mixed salts.[453−455]

Attempted copolymerizations of MMA oligomers with MMA were relatively unsuccessful. Rather, the MMA oligomers served as chain-transfer agents. The chain-transfer activities of a series of MMA oligomers were evaluated in MMA polymerizations over the temperature range 45−100 °C.[456] The transfer constants were determined by analysis of the chain length distributions of the resulting polymers as a function of macromonomer concentration. The MMA dimer was substantially less effective as a chain-transfer agent than the MMA trimer or the higher macromonomers. At 60 °C, the constants were 0.013 for dimer, 0.19 for trimer, 0.31 for tetramer, and 0.21 for mixed higher oligomers with an average DP of 24. The transfer constants demonstrated only a small temperature dependence and no variation with conversion. There was no discernible retardation in the rate of polymerization. A reduced yield of polymer was observed. In bulk polymerizations with conversions greater than 10%, the reduced yield was attributed to the absence of the gel (Trommsdorff) effect. The results are interpreted in terms of the addition−fragmentation mechanism for chain transfer shown in Scheme 14.[457]

Scheme 14. Mechanism of Addition−Fragmentation Chain Transfer



Thermal degradation of the oligomers as a model for the transfer process indicates that the process is homolytic bond cleavage and not a retro-ene reaction.[458]

MMA oligomers are effective chain-transfer agents in a variety of copolymerizations.[337,459−461] If the dimer of hydroxyethyl methacrylate is employed as a chain-transfer agent in MMA polymerization, the resulting product is an α,ω-telechelic polymer.[462] It was noted that the chain-transfer constant was dependent upon the concentration of the dimer. Emulsion copolymerization of MMA oligomer which was essentially trimer with butyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, methacrylamide, and methacrylic acid gave a latex with average particle diameter of over 100 nm and a molecular weight reduced significantly from that which would have been obtained without the trimer.[337] The dimer of methacrylic acid is useful for control of molecular weight in emulsion polymerizations.[463]

Other dimers that have been employed are those of methacrylic acid and its anhydride,[464] ethyl methacrylate, methacrylonitrile, and α-methylstyrene.[465,466] The cross dimers of these monomers with each other as well as with MMA were also found to be effective, with those species containing α-methylstyrene being particularly effective.

The dimer of α-methylstyrene is useful in controlling molecular weight in polystyrene manufacture.[467,468] The control of molecular weight with

malodorous sulfur compounds is particularly important in room-temperature-curable hand lay-up molding and spray-up molding applications.[469] In dental adhesives which are cured by UV irradiation, the presence of α-methylstyrene dimer controls hardening time and the heat of polymerization.[470]

Polymers incorporating AMS dimer are utilized in a number of aspects of paper making. It is desirable to maintain as much of the fiber from the paper pulp as possible in the paper rather than in the wastewater. These polymers must demonstrate thickening at low shear ratio and good flowability at high shear ratio. A copolymer of Et acrylate, methacrylic acid, and poly(ethylene glycol) acrylate palmityl ether prepared utilizing AMS dimer in a chain-transfer polymerization performed well as a fiber retention agent.[471] To enhance the surfactant properties of these polymers, other useful monomers include sulfonates of vinyl-terminated polyalkyleneglycols and vinyl-terminated alkylpolyalkylene glycols. Surface properties of the paper are particularly important in printing, and the molecular weight of latex polymers containing acrylamide, acrylic acid, acrylonitrile, butadiene, itaconic acid, MMA, and styrene are controlled with AMS dimer.[472]

After the paper making process is complete, latexes that are useful as binders for the application of clays or $CaCO_3$ to paper for printing paper may be prepared using the dimer of AMS. In a typical formulation, styrene, butadiene, Me methacrylate, and acrylonitrile were emulsion polymerized in the presence of AMS dimer to obtain a copolymer latex.[473] Surprisingly, the AMS dimer was used in combination with *tert*-dodecylmercaptan, so there may have been some residual odor. Unsaturated carboxylic acids, such as acrylic acid, or sulfonic acids, such as 2-ethylsulfonyl acrylate, or unsaturated amides, such as acrylamide, are also useful, providing the polarity necessary in these applications.[474]

The dimer of AMS is used in the preparation of waterborne coatings.[475] When used to control molecular weight in copolymerizations of diacetone acrylamide, acrylic acid, MMA, MA, and BA with a Na vinylsulfonate copolymer ammonia salt, the resulting waterborne coating shows good gloss and excellent resistance against water, salt-spray, and blistering. Similar systems are utilized for can coatings.[476] When the polymers are going to be used in food applications, it is particularly important that they be low odor. Therefore, it is useful to replace mercaptans with AMS dimer.[477]

Polymerization of *N*,*N*-dimethylaminopropylacrylamide with AMS dimer gave a polymer useful in the preparation dispersant polymers for black pigmented inks for ink-jet applications.[478−481] In one, the polymerization was initiated with 2,2′-azobis(2-methylpropioamidine) dihydrochloride in a water−2-propanol mixture, and it is likely that the spent catalyst was extracted into the aqueous phase.[478] The inks demonstrate good storage stability. Imide and urea functionalities are also incorporated into polymers for dispersants utilizing CCT technology.[482]

Powder coatings are an important step toward the lowering of volatile emissions from painting operations. Polymers for automotive finishes typically contain methyl methacrylate, butyl methacrylate, and glycidyl methacrylate. Incorporation of AMS dimer into one of these polymerizations yields polymers of the proper molecular weight which are free from the odor problems associated with thiol chain-transfer agents.[483,484] Formulation into a powder coating gave a product with little yellowing.

Formulation of poly(vinyl chloride) into sheet goods is often beset with color problems. The kneading process takes place in the presence of dibutyltin maleate to initiate cross-linking reactions. The presence of AMS dimer in the kneading process leads to less yellowing and better thermal stability for the PVC sheet.[485]

AMS dimer was used to prepare a macromonomer of 2-ethylhexyl methacrylate. Copolymerization of the resulting macromonomer with butyl acrylate and acrylic acid gave a polymer backbone with T_g less than 10 °C that is useful in adhesive applications.[486] The adhesive is better than the same composition made without the intermediacy of the macromonomer.

Control of molecular weight and branching can also be an issue in the preparation of ABS (acrylonitrile, butadiene, styrene) rubbers. AMSd is employed to lower molecular weight, and the functional end groups may be reincorporated into the polymer to yield branching.[487]

In the copolymerization of difunctional acrylics to prepare cross-linked amorphous glasses for lenses, it is useful to control molecular weight utilizing the AMS dimer. For instance, copolymerization of diallyl isophthalate, dibutyl maleate, and diethyleneglycol bis(allyl carbonate) in the presence of AMSd in a mold gave a lens showing good refractive index, transparency, and impact resistance.[488] Similar results are obtained for metal-containing optical coatings based upon neodymium in di(2-methacryloyloxyethyl)phosphate, mono(2-methacryloyloxyethyl)-phosphate, methacrylic acid, and phenoxyethyl acrylate. The resulting antiglare coatings are very moisture resistant.[489]

The compound 3,9-divinyl-2,4,8,10-tetraoxaspiro-[5.5]undecane together with a peroxide is utilized in the cross-linking or curing of polyethylene for wire and cable applications. Addition of 2,4-diphenyl-4-methyl-1-pentene (AMSd) inhibits scorch or premature cross-linking of the polymer, presumably through interception of the radicals.[490]

Apparently, AMSd is also useful in the reduction of the molecular weight of waste polymer.[491] Heating polystyrene foam pieces recycled from food packaging materials at 160 °C for 1 h in the presence of AMSd reduced the M_n from approximately 70 000 to 10 000. The mode of action is unknown, but it is presumed that AMS radicals are generated and abstract hydrogen atoms from the polystyrene backbone, resulting in chain cleavage.

In a more esoteric application, the dimers are useful in the study of free-radical chemistry through trapping experiments.[351,352]

5.2. Macromonomers for Graft Copolymers

In some instances, the macromonomers synthesized by CCT can be copolymerized with acrylics to form comb copolymers. While β-scission predominates in copolymerizations with methacrylates, acrylates and styrene give both incorporation to yield comb copolymers and β-scission.[492] Products of this type have been thoroughly characterized by a variety of spectroscopic techniques. When high levels of CCT macromonomers are employed, it is possible to go beyond the comb structure and obtain more highly branched polymers.[493]

In a more specific example, macromonomer composed of *n*-butyl methacrylate and methacrylic acid prepared by CCT was copolymerized with *n*-butyl acrylate containing a small portion of methyl methacrylate.[341] Comparison to the equivalent copolymer made with a macromonomer prepared with a thiol chain-transfer agent demonstrated that the CCT macromonomer formed a copolymer while the thiol macromonomer did not. When these compositions were cured using trifunctional isocyanates, they were useful as both clear and pigmented automotive finishes.

Dispersions of organic or inorganic particles that are insoluble in the liquid vehicle are stabilized by polymeric dispersants. These dispersants are usually structured polymeric systems (random, block, or graft) having at least one segment that is soluble in the vehicle and at least one segment that is insoluble in the vehicle and having an affinity for the particle. They have improved stability when the insoluble segment contains cross-linkable groups. One or both segments can be prepared by CCT.[494−495]

Core−shell microgels can be prepared utilizing CCT macromonomers[496] and self-stabilized cross-linked latexes.[497−501]

Methyl methacrylate macromonomers were copolymerized to provide a hydrophobic graft on an otherwise hydrophilic polymer.[502,503] Such systems are useful in the preparation of soft contact lenses. Hydrophobic methyl methacrylate macromonomers were synthesized by CCT and subsequently copolymerized with any of the hydrophilic monomers *N*,*N*-dimethylacrylamide, 2-hydroxyethyl acrylate, or *N*-vinyl-2-pyrrolidone by γ-radiation to yield xerogels. The copolymerization was confirmed by NMR analyses and by subsequent aqueous extraction of the resultant copolymers. On swelling in deionized water, hydrogels were formed that had significantly higher Young's moduli than hydrogels based on random copolymers of equivalent composition

Polar polyacrylamide with well-defined nonpolar polystyrene grafts (PAM-*g*-PSt) was synthesized via macromonomer technique.[504] The resulting amphiphilic polymers exhibit good emulsifying properties. Interestingly, when PAM-*g*-PSt was blended with PMAA grafted with PMMA, an intermolecular complex membrane was formed. The permeability of the membrane is controlled reversibly by changing the pH value, making it a chemical valve.

Oligomers of acrylic acid having a DP below 50 are useful as detergent additives and boosters.[388] When employed in subsequent polymerizations, the resulting multiblock copolymers can be neutralized to form ionomeric networks.

Graft acrylic polyols for two-component polyurethane coatings can be prepared by free-radical copolymerization of MMA, BMA, BA, acrylic acid, HEMA, and PMMA macromonomers.[505] The polymers offer an advantage over conventional resins with respect to the application/appearance of coatings as well as the final film properties. Some of these advantages were higher solids and a better control of the coating rheology, an increase in the cross-linking reactivity of the polyols with polyisocyanate, and improvement in film toughness. The change in the morphological structure of the films under tensile stress was of particular interest.

In an alternative approach, chloride-containing polymers such as styrene-*co*-chloromethylstyrene were grafted with MMA by initiating from the chloro groups with chlorocobaloxime.[506,507] Similar reaction had been noted under photochemical conditions, but the reactions can also be run thermally. The mechanism is unclear, but improved polymerization in the presence of zinc as a reducing agent suggests that Co^{I} may have been involved. Polymerization was also initiated from halide donors such as chloroform or trichloroethane without the reducing agent.

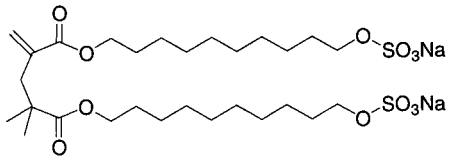
5.3. RAFT

RAFT (reversible addition−fragmentation transfer) polymerization is gaining popularity as an alternative to living polymerizations for the synthesis of narrow molecular weight or structured polymers.[508−514] Early work in the area demonstrated that the methacrylate oligomers synthesized by CCT can be employed in the RAFT process,[512,515] as can dimers of α-methylstyrene prepared cationically.[350] Today, RAFT technology is dominated by the use of thiocarbonylthio compounds and the term RAFT has come to imply the use of these compounds. The RAFT process, very similar to that shown in Scheme 14, involves a series of reversible addition−fragmentation steps.[508,509] Addition of a propagating radical to an MMA oligomer gives an adduct radical which can fragment to form terminated polymeric chain and a new radical. The reaction of the new radical with a monomer (M) results in a new propagating radical. Subsequent addition−fragmentation steps allow a dynamic equilibrium to be established between the active propagating radicals and dormant polymer such that there is an equal probability of growth for all chains, resulting in an apparent living polymerization and a narrow molecular weight distribution.

CCT of benzyl methacrylate leads to a mixture of poly(benzyl methacrylate) macromonomers from which the dimer macromonomer could be isolated.[516] When the benzyl dimer is used as a RAFT chain-transfer agent, PMMA with α- and ω-terminal benzyl methacrylate units is obtained. Catalytic hydrogenation of the α,ω-benzyl terminal methyl methacrylate polymer results in the evolution of toluene and formation of α,ω-dicarboxyl functional telechelic PMMA.

When it is important that surfactants utilized in free-radical emulsion polymerization not be free to

migrate through the polymer in the final application, it is possible to incorporate species such as **116** into the polymerization through RAFT.[517]



116

An MMA dimer obtained by CCT was hydrolyzed and then re-esterified with 1,10-decanediol. The resulting diester was allowed to react with chlorosulfonic acid to produce the methacrylate dimer surfactant, 2,4-bis(sodium 10-sulfate decanoxycarbonyl)-4-methyl-pent-1-ene. At the beginning of a polymerization, the molecule acts as a surfactant and subsequent incorporation of the dimer in the polymerization yields a surfactant-functionalized polymer. Thus, additional surfactants are not required.

5.4. Copolymerization (Graft-Copolymers)

Branched acrylic polymers based upon the copolymerization of acrylates and related monomers with methacrylate macromonomers are particularly useful in waterborne coatings. A macromonomer based upon isobutyl methacrylate, 2-ethylhexyl methacrylate, and 2-hydroxyethyl methacrylate was copolymerized with butyl acrylate, 2-hydroxyethyl acrylate, methacrylic acid, methyl methacrylate, and styrene.[518] After neutralization with dimethylethanolamine or inorganic bases, the polymer could be cross-linked with melamine resin on a metal surface. These systems may be used for either pigmented layers or clear coats.

5.5. Hyperbranched and Cross-Linked Materials

Much of the material in this section was already covered under polymerizations of di- and triacrylates in section 4.1.1.

Copolymerization of di- and trimethacrylates with functionalized monomers, like glycidyl methacrylate, leads to low-viscosity oligomers capable of nonradical cross-linking. This process promises substantial value for industrial applications. Star polymers useful in coatings were prepared by copolymerizing methacrylate macromonomers with diacrylates.[519] For instance, a star polymer was synthesized by copolymerization of a 2-ethylhexyl methacrylate/isobutyl methacrylate/hydroxyethyl methacrylate macromonomer with butanediol diacrylate.

6. Conclusions

Catalytic chain transfer is a versatile tool that complements other means of polymerization. It allows the synthesis of the large variety of structured polymers shown in Figure 11. The primary outlet for CCT is to control molecular weight in free-radical polymerizations without the use of stoichiometric chain terminators (sections 1−3). All of the products can be considered to be monofunctional in that they are all terminated by unsaturation. The unsaturation

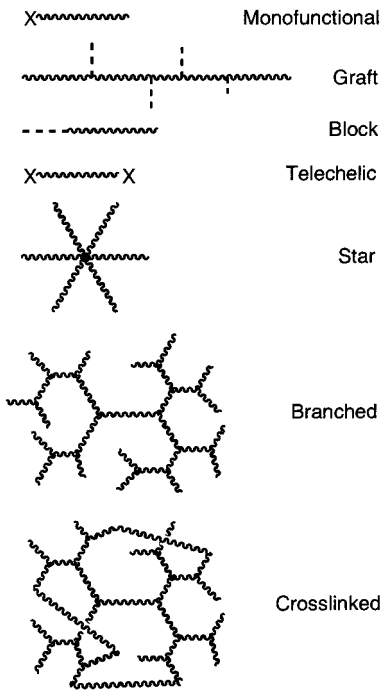


Figure 11. Polymer structures available through CCT.

is largely olefinic in nature but can also be aromatic or aldehydic through isomerizational CCT (section 4.9). In what would appear to be a homeopathic application, the products of CCT themselves, free of cobalt CCT catalyst, can be used to control molecular weight through RAFT (section 5.1).

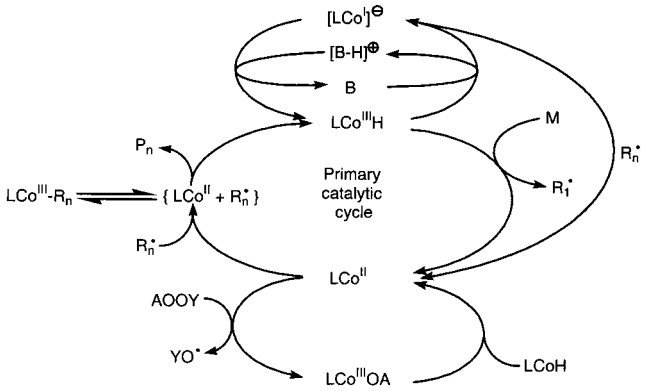
If functionalized macromonomers are utilized in RAFT with nonfunctionalized monomers, the resulting polymers may be telechelic in other polymerizations (section 5.3).

It is interesting that the bulk of products prepared by CCT go into applications where aesthetics are important. The most widely practiced application for CCT polymers is in automotive and other higher technology finishes. In these applications, polyfunctional polymers are cross-linked to provide tough, impermeable finishes with good aesthetics (section 4.1). Copolymerization of the olefinically unsaturated macromonomers with smaller monomers such as acrylates leads to graft copolymers (section 5.4). If the large macromonomers are copolymerized with a minimal amount of comonomer, the resulting polymer is more like a star, but incorporation of macromonomers into macromonomers leads to branched and hyperbranched systems (sections 4.10 and 5.5). CCT polymers find utility in paper and printing technologies only in the higher end applications—making paper where high quality is demanded or making inks and pigments for high-quality printing.

Only complexes having an unpaired electron can operate as CCT catalysts with the low activation energies or high rates required for this process because only they have essentially zero activation energies for reactions with the growing radical chains.

The abstraction of a hydrogen atom from a growing radical chain by a paramagnetic metal center is analogous to the disproportionation reaction between two radical chains in a normal free-radical polymer-

Scheme 15. Chemical Reactions of Cobalt Chelates under Conditions of Free-Radical Polymerization



ization. The major difference is that the metal centers do not interact with each other, so concentrations considerably higher than those that can be obtained with organic radicals are possible.

The one-electron oxidative addition of a radical center to a metal center to form a M−C bond is analogous to the coupling of two radicals to form a C−C bond in a free-radical polymerization. This transformation is not along the reaction coordinate of CCT and can be a serious competitive reaction.

Scheme 15 summarizes the current understanding of LCo in free radically polymerized vinylic monomers. It differs from the previously available scheme[25] in that the formation of the radical adduct with LCo is not the first step of CCT but rather is a reaction that poisons the catalyst. Second, the scheme includes catalytic termination arising through the reaction of LCo^{I} with radical chains. Its should be emphasized that essentially all of the reactions are substantially reversible. The directions of the arrows indicate the course of productive transformations.

7. Glossary

A	anionic ligand coordinated to cobalt
AIBN	azobis(isobuteronitrile)
AMS	α-methylstyrene
BA	butyl acrylate
BMA	butyl methacrylate
C_C	chain-transfer constant to monomer, where $C_C = k_C/k_P$
$C_{C(n)}$	C_C for each radical (when DP is considered)
CCT	catalytic chain transfer
C_M	chain transfer to monomer rate constant, where $C_M = k_M/k_P$
DABCO	diazabicyclo[2.2.2]octane
DP_n	number-average degree of polymerization
DP_w	weight-average degree of polymerization
DP_{n0}	number-average degree of polymerization when no chain-transfer agent is added
DP	degree of polymerization of a monodisperse fraction (applied when the reactivity of each radical is different)
EHMA	ethylhexyl methylacrylate
Et	ethyl
EWG	electron withdrawing group
HEMA	hydroxyethyl methacrylate
HMPA	hexamethyl phosphorustriamide
iCCT	isomerizational catalytic chain transfer
LRP	living radical polymerization
MA	methyl acrylate
LRP	living radical polymerization
MAN	methacrylonitrile
MAn	maleic anhydride
MBL	α-methylenebutyrolactone
Me	methyl
MMA	methyl methacrylate
Por	porphyrin
Pht	phthalocyanine
Py	pyridine
R	radical
R_1	primary radical, obtained by addition of hydrogen to a monomer
R_n	polymeric radical with degree of polymerization of *n*
RAFT	reversible addition−fragmentation transfer
St	styrene
VP	vinyl pyrrolidone
W	rate of polymerization

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