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Dependence of Free-Radical Propagation Rate Constants on the Degree of Polymerization

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ABSTRACT: Cobalt-catalyzed chain transfer in methyl methacrylate (MMA) or methacrylonitrile (MAN) polymerizations employing very high concentrations of catalyst allows the detailed investigation of the reaction of primary radicals with monomers. The enabling reaction is the transfer of a hydrogen atom from a Co(III)−H species to monomer to generate the monomer radicals (H-MMA$^•$ and H-MAN$^•$, respectively). These radicals react with additional monomer yielding the dimer radicals, H-MMA$_2^•$ and H-MAN$_2^•$, respectively, or with the cobalt catalyst to yield the starting monomer. These reactions generate the respective dimers relatively free of higher oligomers. This approach has allowed the determination of the rates of reaction of the monomer radical (k_{p1}) and dimer radical (k_{p2}) with monomer. H-MAN$^•$ reacts with methacrylonitrile at a rate ($k_{p1} = 340 \pm 40$ M^{-1} s^{-1} at 60 °C) which is considerably faster than does a high polymer radical (literature: $k_{p\infty} \equiv k_p = 55$ M^{-1} s^{-1} for MAN at 60 °C). For H-MMA$^•$ at 60 °C, $k_{p1} = 14\,000 \pm 1500$ M^{-1} s^{-1} and for H-MMA$_2^•$, $k_{p2} = 3600$ M^{-1} s^{-1}, relative to the literature value for H-MMA$_\infty^•$, $k_p = 843$ M^{-1} s^{-1}. It was also possible to determine the rate constants of catalytic chain transfer by the cobalt catalysts; in MMA free-radical polymerization at 60 °C, $k_{s2} = 2.3 \times 10^6$ M^{-1} s^{-1} for the tetramethyl ether of [hematoporphyrinato IX]cobalt(II) and 2.8×10^6 M^{-1} s^{-1} for [tetra(*p*-methoxyphenyl)porphyrinato]cobalt(II).

Introduction

The fundamental reactions of radical species impact both polymer chemistry and organometallic chemistry. These transformations include the reactions of primary radicals derived from initiators with monomers as well as reactions of their derivative oligomeric or polymeric radicals with additional monomers. In addition, there is growing interest in the reactions of these species with organometallic complexes, either in chain transfer catalysis[1] or living radical polymerizations.[2]

It is generally accepted that the values of propagation rate constants for free-radical polymerization change as a function of radical length at low degrees of polymerization but that the propagation rate constants become constant after the number degree of polymerization reaches some value where the radical center is no longer influenced by the other chain end.[3] It is this constant value that is referred to as the rate of propagation. Several publications support the notion that small radicals add to double bonds 1−3 orders of magnitude faster than high-polymeric radicals.[5] There are numerous publications which demonstrate that relative rate constants for addition are sensitive to substituents on both the radical center and on the olefin undergoing addition.[6] It is therefore evident that results obtained with model systems should be applied to polymerization systems with caution.

Actual experimental observation of the dependence of propagation rate constants on the length of the radical has been limited.[7] The major limitation in measuring propagation rate constants for short radicals has been the difficulty of specifically generating radicals of a particular length, *N*, while minimizing propagation of the ($N + 1$) radical. Computer simulation of the experimental molecular weight distribution partially overcomes this problem[8] but leads to new uncertainties inherent in that method.

With the discovery of catalytic methods for the control of molecular weight in free-radical polymerizations,[9] the dependence of the propagation and termination rate constants on radical length is becoming of practical importance. Because chain transfer catalysis (CTC) allows one to obtain polymers and oligomers with molecular weights of a few hundred, the effects of chain ends are a substantial factor—the extremely high efficiency of CTC shifts the polymerization into this underinvestigated but fertile area of rate constant dependence on radical length.

In this paper, we will discuss the direct experimental observation of radical-length-dependent rate constants made possible by applying techniques that have become available recently. The approach is based upon chain transfer catalysis (CTC) employing cobalt organometallics. It provides a direct method for dramatically limiting the degree of polymerization from high polymer to dimer, without substantial alteration of the other reactions of polymerization. CTC is normally a convenient synthetic method, but in the limit, it can become a useful analytical tool. Smirnov was the first to recognize the new opportunities for kinetic measurements under CTC conditions,[7b] having found that the chain transfer constants, C_s ($C_s = k_s/k_p$), change in the sequence $R_{>5} \geq R_4 > R_3 > R_2$. This conclusion was drawn from the analysis of the relative concentrations of each oligomer in the CTC product. Because C_s is a ratio of the chain transfer and propagation rate constants, it was impossible to ascertain which of these two factors played the greater role in the observed trend or whether these two factors varied in parallel or opposite directions. Simultaneous change of both k_s and k_p could possibly lead to invariant C_s.

Free-radical polymerization of a single monomer under conditions of chain transfer catalysis can be described by Scheme 1. The first three equations present a simplified version of the basic reactions of free-radical polymerization—initiation, propagation, and termination. In (1), the initiator decomposes to yield free radicals capable of initiating polymer chains. In (2), radical species containing *n* monomers grow by one monomer. In (3), two radical species encounter one

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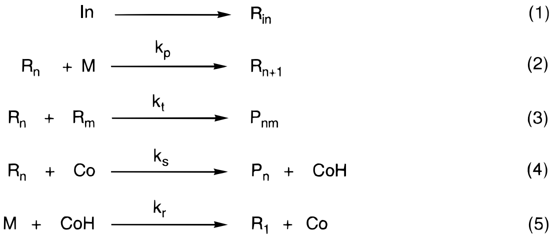
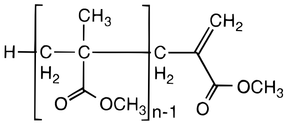
Scheme 1



another to terminate the radical chains. In the example given, this occurs by radical−radical combination, forming a polymer chain $n + m$ monomers long. Bimolecular disproportionation to form a saturated polymer chain and an unsaturated polymer chain is another important termination step, but in this work, it is only the fact of termination and not the method by which it occurs which matters. Reactions 4 and 5 describe chain transfer catalysis. The polymeric radical R_n reacts with the cobalt(II) catalyst (Co), usually a cobalt(II) chelate like cobalt porphyrin, cobalt phthalocyanin, or cobaloxime, yielding a cobalt(III) hydride and a polymer molecule P_n. In the particular case of methyl methacrylate polymers or oligomers, the molecule, P_n, consists of exactly n molecules of methyl methacrylate and has a terminal double bond, as shown in **1**. The cobalt hydride reacts with additional monomer to yield R_1, regenerating the Co(II) catalyst. According to eqs 1−5 the chain transfer catalyst could be considered to be only a device for the transfer of hydrogen atoms from radicals to monomers. It does not influence any other reactions of the free-radical polymerization. Another important feature of CTC is the unique structural homogeneity of the radicals and polymers formed. Even the smallest polymeric molecules, dimers, consist exactly of two monomer units; at high turnovers, there is no trace of the initiator radicals. No other method produces small radicals of such a uniformity.



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Method

Generally, the reduction of polymer molecular weight by CTC does not change the molecular weight distribution of the products which remains close to 2.[9a−c] The number average degree of polymerization, $\overline{\mathrm{DP}}$, under CTC conditions depends upon the concentration of the chain transferring agent according to the Mayo equation (6)

$$\frac{1}{\overline{\mathrm{DP}}} = \frac{1}{\overline{\mathrm{DP}}_\infty} + \frac{k_s[\mathrm{S}]}{k_p[\mathrm{M}]} \tag{6}$$

where $\overline{\mathrm{DP}}_\infty$ is a number average degree of polymerization obtained in the absence of a chain transfer agent, S, and [M] is the concentration of the monomer if $\overline{\mathrm{DP}} > 20$. The situation begins to change as $\overline{\mathrm{DP}}$ is reduced to less than 20 units; the $\overline{\mathrm{DP}}$ decreases more slowly than predicted by the increase in [S]. Because the traditional form of the Mayo equation (6) is based upon the assumption of long chains, it cannot be utilized to explain the observed deviations from the expected dependence of the degree of polymerization on the concentration of a chain transfer agent.[7b] A high concentration of catalyst will lead to intensive chain transfer and consequently short polymer chains. It has been reported[9f] that under these conditions, the Mayo equation reduces to

$$\overline{\mathrm{DP}} = 2 + \frac{k_p[\mathrm{M}]}{k_s[\mathrm{S}]} \tag{7}$$

This form of the equation is based upon the assumption that k_p and k_s are independent of the length of the radical chain. We will demonstrate that these assumptions are incorrect, but nonetheless, eq 7 provides a better description of the products obtained under high catalyst concentrations than does eq 6. Mathematical derivations for these conditions[9f] together with supporting experimental data,[7b] indicate that when $\overline{\mathrm{DP}}$ is less than or equal to about 10, the polydispersity should begin to decrease from 2, reaching a value of 1 for $\overline{\mathrm{DP}} = 2$. This occurs solely for kinetic reasons and the definitions utilized. At very high levels of catalyst, all of the radicals in the polymerization mixture are either R_1 or R_2. Addition of more catalyst lowers the concentration of dimer radicals, R_2, and other higher radicals and increases the concentration of monomeric radicals, R_1. Essentially, the radicals become nonproductive and polymerization is inhibited. Due to the high efficiency of cobalt-catalyzed CTC, the concentrations of cobalt required to make almost exclusively R_1 radicals in the reaction mixture are easily achieved. The primary product of CTC under such conditions is P_1, the monomeric product, which is indistinguishable from an unreacted monomer except through isotopic exchange studies.

Calculations from an earlier paper[10] indicate that the total concentration of radical species in the reaction mixture should remain relatively constant even as the concentrations of individual species change. For a given rate of radical production, the termination rate constants determine the radical concentration by the well-known dependence $V = k_{ti}[R_i]^2$, where V is the rate of reaction 1. It is generally accepted that the value of k_{ti} depends mostly on the rate of diffusion of the radicals R_i and the rate of diffusion is controlled by radical size.[11] We choose conditions for our experiments to give predominantly only radicals from R_1 to R_4. Radical R_1 remains the radical species of highest concentration. Under such conditions, the main termination reaction for all other radicals is a recombination with R_1. Because R_1 is the most rapidly diffusing species, we can expect that the rate constant of the termination for all radicals is equal to k_{t1}. Therefore, in this system the sum of all radical species should be essentially constant at each value of V.

As the rate of chain transfer catalysis increases, the steady-state partial concentrations of R_1 should increase until R_1 would be virtually the only radical species in the reaction solution. Further increase of the catalyst concentration should not influence the concentration of R_1 which is determined only by k_{t1}. In a preceding paper[12] it was shown that at very high cobalt concentrations, the concentration of Co(III)−R_1 increases with an increase of overall concentration of cobalt chelate while the concentration of the monomer radical is independent of cobalt concentration.

R_1 is the only radical species of any appreciable concentration and its primary reaction is β-hydrogen elimination by means of pathway (4). Nonetheless, there remains a possibility that R_1 will react with additional monomer to form R_2. Hence, under intensive CTC the R_2 radical should be produced at a constant rate dependent only on the concentration of radical and monomer:

$$\mathrm{R}_1 + \mathrm{M} \xrightarrow{k_{p1}} \mathrm{R}_2 \tag{8}$$

In eq 8, k_{p1} is the propagation rate constant for the radical R_1. The high concentration of CTC catalyst would cause the radical R_2 to be immediately converted to P_2 by reaction 4. The rate of dimerization would be therefore limited not by the chain transfer reaction but by the propagation reaction of R_1.

$$\frac{d[P_2]}{dt} = W_2 = k_{p1}[M][R_1] \qquad (9)$$

Equation 9 allows the calculation of k_{p1}. The concentration of radicals R_1 can be obtained from eq 10.

$$[R_1] = \sqrt{\frac{V}{2k_{t1}}} \qquad (10)$$

The constant, k_{t1}, is the bimolecular termination rate constant for radical $R_1$and V is rate of reaction 1, which is easily measured by trapping the initiating radicals with stable free radicals.[13] Therefore we can obtain k_{p1} through measurement of k_{t1}.

If we decrease the concentration of the catalyst incrementally, the rate of CTC will decrease until the radical R_2 reaches concentrations where it will be able to propagate the chain further to yield radical R_3 but not R_4. Under such conditions, essentially only dimers and trimers will be formed as products. Then the steady-state concentration of the radical R_2 is given by (11).

$$\frac{d[R_2]}{dt} = k_{p1}[R_1][M] - k_{p2}[R_2][M] - k_{s2}[R_2][Co] \approx 0 \qquad (11)$$

For these defined conditions, the rate of dimer formation, W_2, and the rate of trimer formation, W_3, are

$$W_3 = k_{p2}[R_2][M] \qquad (12)$$

and

$$W_2 = k_{s2}[R_2][Co] \qquad (13)$$

Therefore eq 11 could be rewritten as

$$[R_1] = \frac{W_2 + W_3}{k_{p1}[M]} \qquad (14)$$

As noted above, CTC does not change the overall concentration of radicals. Assuming that the concentration of R_3 radicals is negligible relative to that of R_2, we can postulate

$$[R_1] = [R]_o - [R_2] \qquad (15)$$

Substituting eq 15 into eq 14 gives

$$[R_2] = [R]_o - \frac{W_2 + W_3}{k_{p1}[M]} \qquad (16)$$

Substituting eq 16 into eq 12, we obtain

$$k_{p2} = k_{p1}\frac{W_3}{W_2^* - (W_2 + W_3)} \qquad (17)$$

where $W_2^* = k_{p1}[R]_o[M]$ is the rate of dimerization obtained under conditions of higher catalyst concentration so that the dimer is the only product and $[R]_o = [R_1]$ as described by eq 9. Dividing eq 12 by eq 13, we obtain the value of the CTC rate constant for radical R_2:

$$k_{s2} = k_{p2}\frac{[M]W_2}{[Co]W_3} \qquad (18)$$

If we further decrease the rate of the CTC relative to the rate of the monomer addition, tetramer starts to form. If the concentration of the pentamer is negligible, then the steady-state concentrations are defined by the following equations:

$$\frac{d[R_2]}{dt} = k_{p1}[R_1][M] - k_{p2}[R_2][M] - k_{s2}[R_2][Co] \approx 0$$

or

$$[R_1] = \frac{k_{p2}[M] + k_{s2}[Co]}{k_{p1}[M]}[R_2] \qquad (19)$$

$$\frac{d[R_3]}{dt} = k_{p2}[R_2][M] - k_{p3}[R_3][M] - k_{s3}[R_3][Co] \approx 0 \qquad (20)$$

We can choose conditions for

$$W_4 = k_{p3}[R_3][M] \qquad (21)$$

$$W_3 = k_{s3}[R_3][Co] \qquad (22)$$

and

$$[R]_o = [R_1] + [R_2] + [R_3]$$

or

$$[R_3] = [R]_o - [R_1] - [R_2] \qquad (23)$$

Applying eq 23 to eq 21, we will have

$$k_{p3} = \frac{W_4}{[R_3][M]} = \frac{W_4}{[R]_o[M] - [R_1][M] - [R_2][M]}\frac{k_{p1}}{k_{p1}}$$

or

$$k_{p3} = k_{p1}\frac{W_4}{k_{p1}[R]_o[M] - \frac{k_{p1}}{k_{p2}}k_{p2}([R_1][M] + [R_2][M])} \qquad (24)$$

Substituting the concentrations of radicals R_2 with eq 19, and then applying (20)−(22) will finally transform eq 24 into (25)

$$k_{p3} = k_{p1}\frac{W_4}{W_2^* - (W_3 + W_4)\frac{k_{p1}}{k_{p2}}\left(1 + \frac{k_{p2}[M] + k_{s2}[Co]}{k_{p1}[M]}\right)} \qquad (25)$$

A further change in the ratio between the propagation rate and the CTC rate will give rise to pentamer formation but not hexamer. Then hexamer will form, but not heptamer, etc. For each such situation we can determine k_{pN} and k_{sN}.

Applying the same approach as shown above, we obtain general equations

$$k_{pN} = k_{p1}\frac{W_{N+1}}{W_2^* - (W_N + W_{N+1})\frac{k_{p1}}{k_{p(N-1)}}\{1 - \sum_{m=1}^{N-2}(\sum_{q=m}^{N-2}\beta_q)_m\}} \qquad (26)$$

where

$$\beta_q = \frac{k_{p(q+1)}[M] + k_{s(q+1)}[Co]}{k_{pq}[M]} \qquad (27)$$

and

$$k_{sN} = k_{pN}\frac{W_N[M]}{W_{N+1}[Co]} \qquad (28)$$

Equation 26 can be represented for each oligomer formation rate as

$$k_{pN} = k_{p1}\frac{W_{N+1}}{W_2^* - W_2 - \displaystyle\sum_{q=1}^{N-2}\left\{W_{q+2}\sum_{i=1}^{q+1}\left(\frac{k_{p1}}{k_{pi}}\right)_i\right\}_q - W_{N+1}\sum_{i=1}^{N-1}\left(\frac{k_{p1}}{k_{pi}}\right)_i} \tag{29}$$

where $N > 2$ and the $(N + 1)$-mer is the highest molecular weight product formed in the experiment. Therefore, slowly reducing the concentration of the catalyst and measuring the rates of each oligomer formation one could find k_{p1}, then k_{p2}, then k_{s2}, then k_{p3}, then k_{s3}, etc.

Unfortunately, available analytical techniques begin to present a limitation to the technique. NMR spectroscopy does not allow differentiation of the tetramer signal from that of higher oligomers. GPC or HPLC should give more flexibility in the determination of rates by the method described here, but it should be noted that chromatographic quantification of low oligomers requires special calibrations because there are changes in both the refractive indices and UV extinction coefficients with the molecular weight of the oligomers.[14a] Modern mass spectroscopic methods of polymers like MALDI and K$^+$IDS[14b−d] also could be considered.

Experimental Section

Materials. Methacrylonitrile, MAN, and methyl methacrylate, MMA (both from Aldrich), were purified by multiple vacuum distillation immediately prior to use. Deuteriochloroform (Aldrich) was used as a solvent without additional purification. [Tetrakis(*p*-methoxyphenyl)porphyrinato]cobalt(II) or [tetraanisylporphyrinato]cobalt(II), (TAP)Co (Aldrich), was recrystallized twice from chloroform−heptane. The tetramethyl ether of [hematoporphyrinato IX]cobalt(II), HPCo, and [tetramesitylporphyrinato]cobalt(II), TMPCo, were synthesized according to published procedures.[15,16] AIBN (2,2′-azobis(isobutyronitrile)) (Eastman Kodak) was purified by crystallization from chloroform and then ethanol at temperatures below room temperature.

Kinetic Measurements. All reagents were mixed in air and transferred to an ampule or NMR tube adapted for vacuum. After three freeze−pump−thaw cycles (10^{-3} Torr vacuum) the ampules were sealed. After sealing, the NMR tubes were immersed in an isothermal circulating bath at 60 ± 0.1 °C. The degree of dimerization in this was monitored by NMR spectroscopy using a 300 MHz GE spectrometer. NMR measurements were carried out at room temperature. The concentrations of the MAN oligomers were determined by comparison of their vinylic proton signals to that of the monomer. This method, requiring multiple measurements to obtain a single kinetic curve, confirmed the approach but was found to be slow and less accurate than a calorimetric approach.

MMA oligomerization was also studied by isothermal calorimetry. In this case, the prepared ampules were placed in a C-80 (Setaram) isothermal microcalorimeter at 60 °C. The course of the reaction was determined by the exotherm associated with the dimerization reaction. A typical thermogram is shown in Figure 1. After about 1−2 h (conversions of 10% to as high as 40% in cases where high concentrations of the initiator was employed) the ampules were removed, chilled, and opened. The oligomer composition of the reaction mixture was analyzed by proton NMR. Concentrations of monomer and each oligomer were determined by their vinylic proton signals. For oligo-MMA, chemical shifts were taken from the literature.[17] The MAN oligomers were found to have the following vinylic chemical shifts: 5.77 and 5.68 (monomer), 6.12 and 5.95 (dimer), 6.18 and 6.01 (trimer) in chloroform, which correlate well with literature values.[18]

Kinetic Calculations. The initial rate of polymerization, W_{st}, was used as a basic value for all kinetic calculations. In the MAN oligomerization, the rate of formation of all of the oligomers were measured directly by NMR. The value of W_{st} was obtained by extrapolation of the dimerization kinetic curve to the time zero intersection with the y-axis. In MMA oligomerization the value of W_{st} was obtained by extrapolation of the heat flow signal to time zero. The reaction conditions applied in this work were chosen to provide low rates of polymerization so that the heat flow over the first hour decreased linearly with time, facilitating the W_{st} determination.

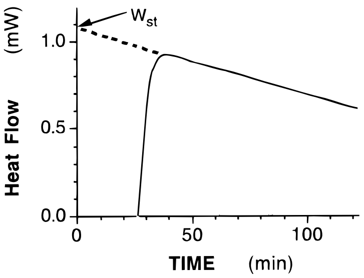


Figure 1. Thermogram of MMA dimerization in a chloroform solution: [MMA] = 0.94 M, 60 °C, [HPCo] = 7.5 × 10^{-3} M, [AIBN] = 0.0133 M.

The heat flow at the beginning of the reaction was then converted to the rate of the MMA dimerization by utilizing the assumption that the heat of dimerization is exactly half that of the heat of polymerization. This assumption is justified because the dimerization process converts the two π-bonds of two monomers into one π-bond and one σ-bond while, in polymerization, each of the π-bonds is converted to a σ-bond. In this case, the heat of MMA dimerization was assumed to be 28.7 kJ/mol (the heat of MMA polymerization was taken as 57.5 kJ/mol).[19] The conversions of several calorimetric runs were checked by NMR after completion, and it was found that agreement was within 10%.

As predicted by eq 7, it was very difficult to obtain the pure dimer as the only product because some trimer forms even when concentration of the chain transfer agent is relatively large in comparison with the concentration of monomer. NMR spectroscopy was able to differentiate between monomer and the individual oligomers up to tetramers. The NMR signals of vinylic protons of pentamers and higher oligomers were not sufficiently separated from the tetramer signal for reliable quantification. We therefore utilized only experimental points with a relatively low concentration of the tetramer to avoid the errors rising from uncertain concentrations of the pentamer and higher oligomers.

The heat of oligomerization is clearly going to be different from that of dimerization or polymerization. Thus, the heat of trimerization will be two-thirds that of polymerization, and the heat of tetramerization will be three-fourths of that of the polymerization. Though the concentrations of these higher oligomers were several times smaller than the concentration of the dimer, they affect the kinetic results obtained by calorimetry because of its superior sensitivity. This effect was corrected by multiplication of the observed initial rate of the polymerization, W_{st}, by the coefficient α defined as

$$W_2 = \alpha W_{st} \tag{30}$$

$$\alpha = \frac{\displaystyle\sum_{i=2}^{i=4}[P_i]}{\displaystyle\sum_{i=2}^{i=4}[(i-1)P_i]} \tag{31}$$

The term W_2 is the initial rate of dimer formation, P_i is an i-oligomer, and $(i - 1)$ is a coefficient which indicates the number of double bonds converted into single bonds during polymerization in the presence of these chain transfer catalysts. Equation 31 allows us to extract the heat (i.e. rate) of the dimerization from the combined heat flow. The denominator in eq 31 shows how many total monomer π-bonds in the reaction mixture convert into σ-bonds, while the numerator shows how many such events are attributed to the formation of dimer only. The rates of formation of the other oligomers were obtained from W_2 by comparison of their vinylic proton

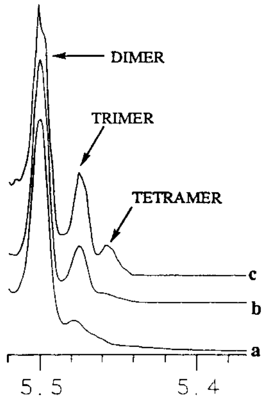


Figure 2. NMR spectra of the MMA-oligomerization reaction products. chloroform solution, [AIBN] = 0.0133 M, [MMA] = 0.94 M, 60 °C. Concentration of HPCo: (a) 10 mM; (b) 3 mM; (c) 0.9 mM.

NMR signals with those of the dimer. It is important to note that trimer and higher oligomers do not originate from reaction of dimer in these reactions which are run at low conversion. Rather, they come from reaction of monomer radicals sequentially with two monomers before interception of the oligomerization process by the cobalt catalyst. Their rate of formation is essentially constant over the course of the reaction.

According to calculations made in an earlier paper,[12] the overall concentration of all radicals, $[\mathrm{R}]_o$, during CTC should be an essentially constant value if their termination rate constants do not differ significantly:

$$\sum_{i=1}^{\infty}[\mathrm{R}_i] \equiv [\mathrm{R}]_o \approx \sqrt{\frac{V}{2k_{t1}}} \qquad (32)$$

We were unable to find references on k_{t1} for methacrylates, but the termination rate constant for the 2-cyano-2-propyl radical (R_1 for MAN) was evaluated by Sustmann et al.[11b] We applied this data to our previous calculations[12] and found the results to be entirely consistent with our assumptions. If k_{t1} depends only on diffusion, as is widely believed, then k_{t1} for MMA should not differ significantly from that of methacrylonitrile, and $k_{t1} \approx k_{t2} \approx k_{t3}$.

According to eq 7, pure dimer free of higher oligomers will be obtained only when the concentration of the catalyst is infinite, and then only at infinitesimally slow rates. Nonetheless, it is relatively simple to obtain dimer with only traces of higher oligomers. Because the ratio of dimer to higher products is determined by the competition of monomer and catalyst for the radical species present, increasing the concentration of catalyst or decreasing the concentration of monomer will give the same result. The lower the concentration of monomer, the more difficult it is to measure the rate of polymerization, especially when the rate of initiation is maintained at low levels to reduce the error in the measurement of W_{st}, so it is preferable to raise the concentration of catalyst. Nonetheless, limitations in the solubility of the catalyst will sometimes dictate the approach. In the example of MMA, propagation rate constants are not limiting, but potential catalyst concentrations are limited by solubility. In particular, TMPCo was found to have low solubility in chloroform, the preferred solvent for porphyrins. By varying both parameters it was possible to obtain sequentially (a) almost pure dimer with less than 5% trimer, (b) dimer with an appreciable concentration of trimer, and (c) dimer with combined concentrations of trimer and tetramer of more than 30% (see Figure 2, correspondingly, a, b, and c). The propagation rate constants of MAN are low compared to MMA and it was found to be easier to tune the experimental conditions to yield essentially pure dimer.

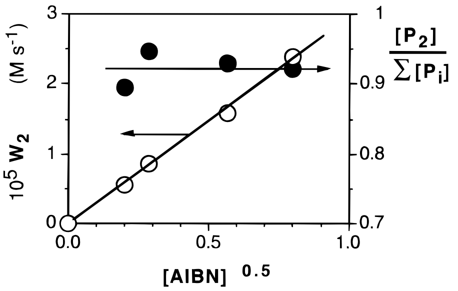


Figure 3. Dependence of the initial rate of MAN dimerization on the square root of the concentration of the initiator: 60 °C, chloroform solution, [TAPCo] = 0.007 M, [MAN] = 1.49 M.

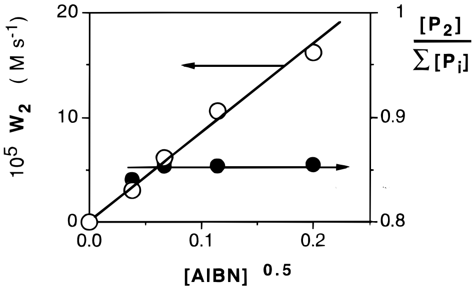


Figure 4. Dependence of the initial rate of the MMA dimerization on the square root of the concentration of the initiator: 60 °C, chloroform solutions, [TAPCo] = 0.0047 M, [MMA] = 0.94 M.

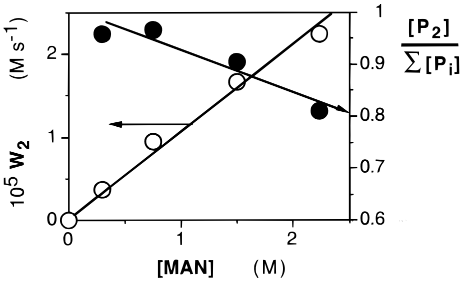


Figure 5. Dependence of the initial rate of the MAN dimerization on concentration of the monomer: [TAPCo] = 0.007 M, 60 °C, chloroform solution, [AIBN] = 0.32 M.

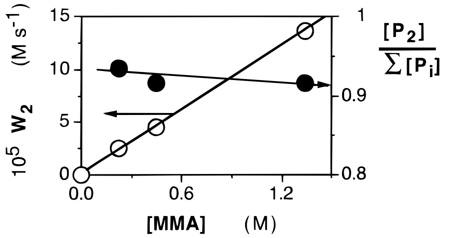


Figure 6. Dependence of the initial rate of MMA dimerization on the concentration of the monomer: [TAPCo] = 0.007 M, 60 °C, chloroform solution, [AIBN] = 0.0133 M.

When the concentrations of higher oligomers are less than ≈30%, the experiments on the dimerization are close enough to the conditions described mathematically above that useful information can be obtained. To provide the reader some idea how far each experimental point is from the "ideal", we provide all plots with an additional *y*-axis, which indicates the partial dimer concentration in the reaction products, $[\mathrm{P}_2]/\Sigma[\mathrm{P}_i]$.

Results

The rate of the dimerization was found to be proportional to the square root of the concentration of the initiator (Figures 3 and 4) and to increase linearly with the concentration of the monomer (Figures 5 and 6). Both of these findings fit the experimental model of dimerization by free-radical polymerization interrupted

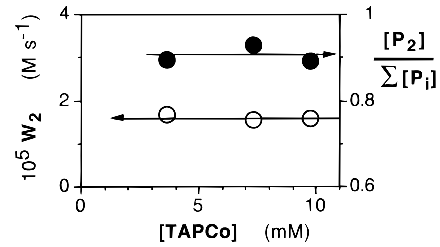


Figure 7. Dependence of the initial rate of the MAN dimerization on the concentration of TAPCo catalyst: 60 °C, chloroform solution, [MAN] = 1.49 M, [AIBN] = 0.32 M.

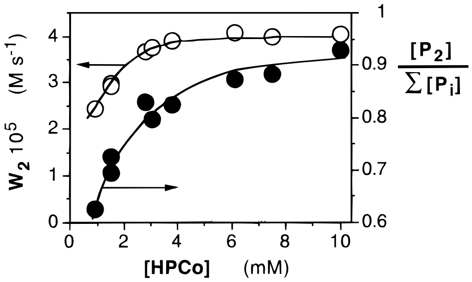


Figure 8. Dependence of the initial rate of MMA dimerization on the concentration of HPCo catalyst: 60 °C, chloroform solution, [MMA] = 0.46 M, [AIBN] = 0.0133 M.

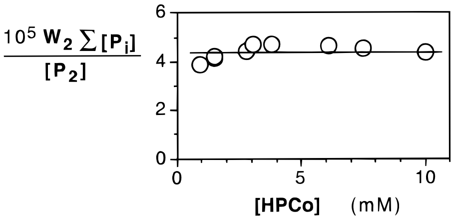


Figure 9. Dependence of the normalized initial rate of MMA dimerization on the concentration of the catalyst. Data are taken from Figure 8.

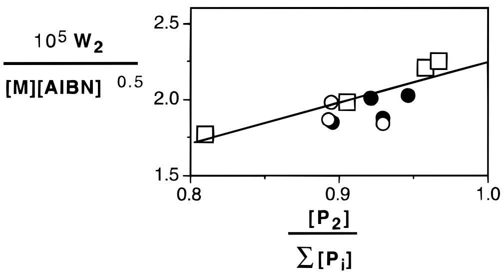


Figure 10. Dependence of the observed propagation rate constant on the partial concentration of the MAN dimer in the CTC products: chloroform solution, 60 °C. The units on the ordinate axis are $M^{-0.5}$ s^{-1}. Experimental data are taken from Figures 3, 5, and 7.

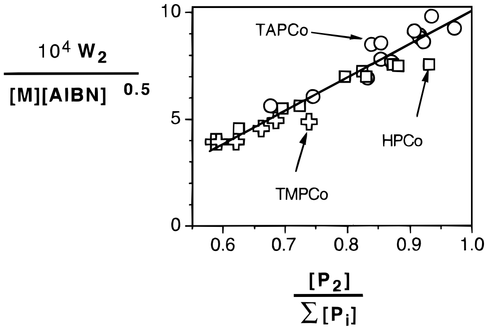


Figure 11. Dependence of the observed propagation rate constant on the partial concentration of the MMA dimer in the CTC products: chloroform solution, 60 °C. The units on the ordinate axis are $M^{-0.5}$ s^{-1}. Experimental data are taken from Figures 4, 6, and 8.

by catalytic chain transfer indicated by eq 9. The rate of dimerization is independent of the concentration of the cobalt porphyrin catalyst (Figures 7 and 8), as it was supposed to be when dimer accounts for at least ≈80% of the reaction products. When the partial concentrations of dimer fall below ≈80%, the conditions of the reaction begin to deviate from the model, indicating that the simplifying assumptions that R_1 is essentially the only radical species present in the reaction mixture, and that $\Sigma[R_i] = [R_1]$ are leading to unacceptably large errors in the calculations (see Figure 8 at $[P_2]/\Sigma[P_i] \leq 0.7$).

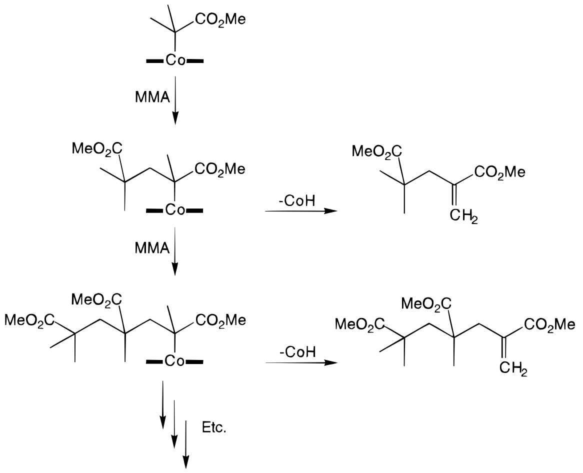
Assuming that the cobalt is equally effective in trapping radicals of different sizes, the resulting partial concentration of radical R_j is proportional to the partial concentration of the P_{j+1}, Figure 9 has been composed by dividing W_2 by the partial concentration of the dimer. The resulting normalized (adjusted) W_2 is relatively independent of the concentration of the catalyst for the lower partial concentrations of the dimer. The deviation from linearity indicates, as can be derived from eqs 26 and 27, that k_p and k_s change with radical length.

All of the experimental points in Figures 3−8 can be used to estimate k_{p1} but in order to obtain average values over a range of experimental conditions, Figures 10 and 11 have been composed. The axes of Figures 10 and 11 allow the combination of all of the data into a single plot independent of the concentrations of catalysts, initiators, and monomers. The dependence of the observed propagation rate constant on the composition of the oligomerization products is seen to be reasonably linear. Despite the fact that conditions where dimer was the sole observed product could not be achieved, an accurate value for the k_{p1} can be obtained by extrapolating the experimental line to the point where the partial concentration of the dimer is 1.0.

The data obtained above allow the calculation of the k_{p1} rate constants for the monomers studied in this paper. Applying the data from Figure 10 (for $P_2/\Sigma(P_i) = 1.0$), eqs 9 and 10, and the data in ref 8b on k_{t1} and V for AIBN in chloroform solutions,[12] we obtain $k_{p1} = 340 \pm 40$ M^{-1} s^{-1} for methacrylonitrile at 60 °C. The intersection of the line in Figure 11 with the y-axis gives an intrinsic k_{p1} for MMA. Then, by a method analogous to that for MAN we calculate the rate constant for the MMA free-radical propagation rate constant, $k_{p1} = 14\,000 \pm 1500$ M^{-1} s^{-1}. Applying those data points that fit the line in Figure 11 to minimize error, we obtain $k_{p2} = 3600$ M^{-1} s^{-1} for MMA at 60 °C by the eq 17. The k_{p1} rate constants for both MAN and MMA are roughly 1 order of magnitude larger than the literature values of propagation rate constants for the corresponding macroradicals ($k_p = 843$ M^{-1} s^{-1} for MMA at 60 °C and $k_p = 55$ M^{-1} s^{-1} for MAN at 60 °C).[20]

Using the data available, it is also possible to determine the chain transfer rate constants, k_s. Applying eq 18, the rate constant k_{s2} was found to be equal to 2.3×10^6 M^{-1} s^{-1} for HPCo and 2.8×10^6 M^{-1} s^{-1} for TAPCo for MMA free-radical polymerization at 60 °C. Both of these values are slightly larger than the rate constants for the corresponding macroradicals and catalysts, 1.42×10^6 M^{-1} s^{-1} for HPCo and 2.4×10^6 M^{-1} s^{-1} for tetraphenylporphyrin−Co, a TAPCo structure analog[9b] ($k_p = 843$ M^{-1} s^{-1} was taken as a propagation rate constant for MMA macroradicals at 60 °C). Therefore the CTC rate constant is much less dependent on the

Scheme 2



(33)

radical length than the propagation rate constant. Perhaps the steric hindrance of the planar porphyrin molecule is great enough to impede reactions with even small molecules. These findings correlate well with Smirnov's data[7b] on C_s variations with radical length.

Discussion

Mechanism of Catalytic Chain Transfer. One must consider the possibility that the dimerization and trimerization reactions studied here occur by cobalt catalysis rather than by means of the mechanism involving free-radical addition interrupted by cobalt-catalyzed chain transfer, which is illustrated in the equations of Scheme 1. It has been suggested recently that CTC is a coordination polymerization taking place by the mechanism shown in Scheme 2.[21]

According to that scheme, a Co–H elimination can occur at any stage of the above coordination polymerization to yield vinylidene-terminated polymer molecules (6). Several observations in the work reported here argue strongly against this proposal.

If the dimerization occurs via a free-radical mechanism, then rate constant k_{p1} should be independent of the nature of the catalyst. Though there are some stray data points in Figure 11, essentially all of the results lay on a straight line for all three cobalt porphyrins utilized in this study. With the variations in steric and electronics of these three porphyrins, it is unlikely that they would catalyze a polymerization at the same rate.

A stronger argument against coordination polymerization is in the observation of variations in the rate of polymerization as a function of the concentration of the cobalt chelate. In a coordination polymerization it would be expected that there would be a direct correlation between the rate of polymerization and the concentration of catalyst. For example, the coordination dimerization (33) would be described by the following two reactions:

$$\mathrm{Co} + \mathrm{R}_1 \xrightarrow{k_x} \mathrm{Co{-}R}_1$$

$$\mathrm{Co{-}R}_1 + \mathrm{M} \xrightarrow{k_y} \mathrm{Co} + \mathrm{P}_2$$

For the steady-state conditions we, then, will have:

$$W_2 = k_x k_y [\mathrm{M}][\mathrm{Co}][\mathrm{R}_1] \qquad (34)$$

Scheme 3

$$\mathrm{Co} + \mathrm{M} \xrightarrow{k_z} (\mathrm{CoM})$$

$$(\mathrm{CoM}) + \mathrm{R}_1 \xrightarrow{k_a} \mathrm{Co} + \mathrm{P}_2$$

The data in Figures 6 and 7 do not support the dependence shown in eq 34. Putting R_N instead of R_1 in eq 34, we obtain the rate of coordination polymerization for high polymer. Available experimental data[9b,c] show that the rate of the polymerization does not change by more than 10% while the concentration of cobalt porphyrin is varied by 2 orders of magnitude. There is, however, a reduction of the molecular weight of the polymer from 200 000 to several hundred. It is clear that any contribution of coordination polymerization into the overall polymerization in CTC is not significant regardless of the MW of the product formed.

To complete the proof of the free-radical mechanism for low-oligomer formation via CTC, one must consider the possibility of monomer activation by complexation with the chain transfer catalyst. This would be illustrated by the reaction in Scheme 3. Scheme 3 leads to the following expression for the dimerization rate:

$$W_2 = k_z k_a [\mathrm{M}][\mathrm{Co}][\mathrm{R}_1] \qquad (35)$$

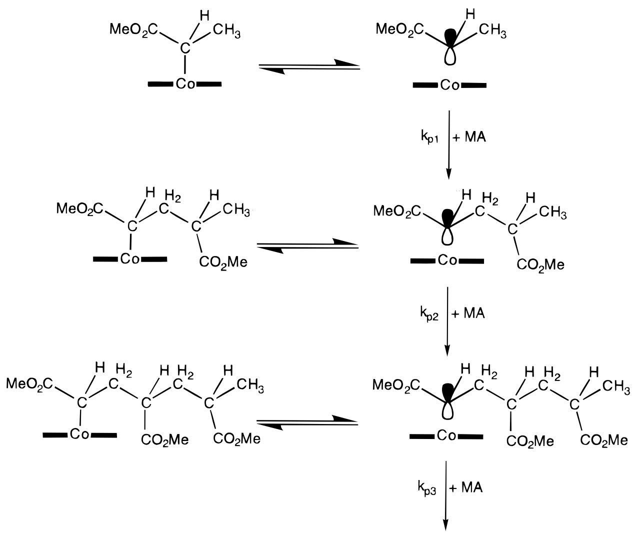
The dependence in eq 35 is essentially the same as in eq 34. Again, one should observe a dependence of the dimer formation rate on the concentration of the cobalt catalyst, which is in contrast with the experimental data of Figures 7 and 8.

Propagation Rate Constants in Living Radical Polymerizations. The techniques presented here provide an interesting opportunity to measure k_p for low molecular weight radicals with monomers which form relatively stable Co–C bonds with a cobalt chelate. These are generally systems in which chain transfer catalysts are less effective—for example, with acrylates. The reported examples of living radical polymerization of acrylates with cobalt chelates as a capping agent[2a,e] require UV irradiation or heating to induce propagation. This indicates that the Co–C bond cleavage could be undertaken under well-controlled conditions. In this case the R_1 radical released via the Co–C bond homolysis can react nonproductively with free Co(II) chelate or add a monomer to form R_2. Due to the persistent radical effect,[22] the primary reaction of both the R_1 and R_2 radicals will be to form organometallic products Co–R_1 and Co–R_2 with little self-termination by reaction 2.

Although other capping agents are well explored for living free-radical polymerizations, cobalt porphyrins or cobalt phthalocyanines will be preferred for the measurement of propagation rate constants in the living radical polymerization shown in Scheme 4. Because of the expanded system of conjugated π-bonds, tetrapyrrolic macrocycles provide ring-current shielding of any axial ligands of cobalt. As a result, many proton signals of axial ligands are shifted upfield to the negative δ region. The well-developed NMR method for identification of axial ligands in Co(II) porphyrins[23] can provide precise quantification of Co–R_N to Co–R_{N+1} conversion for $1 \leq N \leq 3$ with the R_3 end unit proton resonances in the $\delta \approx 0$ region. This range is readily extended by either of two methods.

For monomers which have no protons with chemicals shifts between 0 and 4 ppm (for instance, methyl or benzyl acrylate, acrylonitrile, vinyl formate, or vinyl chloride, but not ethyl and higher acrylates or vinyl

Scheme 4



acetate), the end units of oligomers greater than trimer will lead to proton resonances in the 0−4 ppm region. Quantification by high-resolution NMR will be relatively easy for oligomers of such monomers up to hexamer or even heptamer.

Another approach applicable to essentially all monomers is to initiate the metal-mediated living free-radical polymerization with deuterated monomers. After the degree of polymerization of the axial ligand reaches some desired value, the polymerization is continued with nondeuterated monomer. The next insertion of monomer could be subject to an isotope effect, but all subsequent insertions should be free of any isotope effect and will reflect the propagation rate of that particular *n*-mer plus the observed insertions.

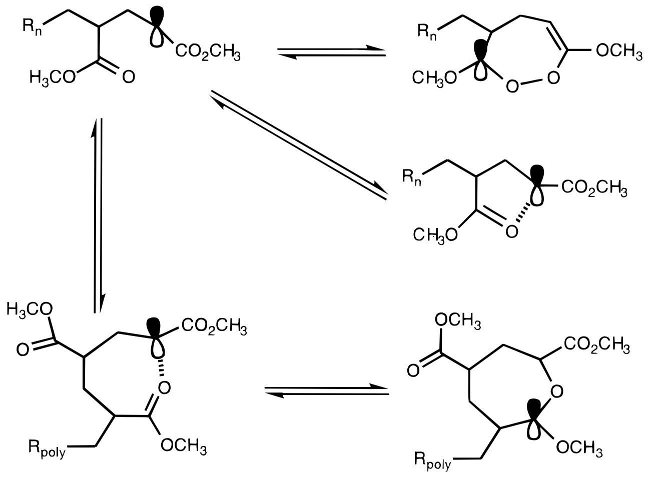
The general equation for the propagation rate constant calculation in these metal-mediated living radical polymerizations is essentially the same as shown above in eqs 9 and 10

$$k_{pN} = \frac{W_{N+1}}{[R_N][M]} = \frac{W_{N+1}}{[M]\sqrt{\dfrac{V}{k_{tN}}}}$$

By definition, the R_N are only those radicals of *N* length that freely diffuse in the reaction mixture. The value of *V* is readily determined by trapping the propagating radicals with stable free-radical traps. The positive feature of this method is that it will provide information on only those radicals which are freely-diffusing but not on caged-radicals if moderate concentrations of the spin-trap are utilized.[24]

The most reliable and readily available results are obtained by this method when the starting organocobalt chelate contains one specific *n*-mer as the organic axial substituent. Although the combination of deuterated/nondeuterated monomer allows the measurement of propagation rates for practically any R_N, the problem of resolution increases with *N* number. Organocobalt porphyrins with secondary C−Co bonds are relatively stable, making them suitable for metal-mediated, living radical polymerization, and they are readily handled at room temperature in air. The bulky, planar, nonpolar, highly chromophoric porphyrin moiety facilitates separation and analysis of these organocobalt porphyrins by liquid chromatography for relatively small R_N. With increasing axial size the difficulties of Co−R_N quantitative separation from any other Co−$R_{N\pm1}$ also increase.

Scheme 5



Uncertainties. One of the more important assumptions made in this method is that the concentration of R_N radicals is negligible relative to that of radicals R_{N-1} when determining k_{pN} by eqs 26 or 29. This is adequate as a first approximation, but for more precise measurements, this assumption would lead to calculated values of k_{pN} smaller than actual because an additional term of R_N must be considered in the equation describing $[R]_o$ (for instance, R_4 in the example of eq 23).

A more significant error could result from the dependence of termination rate constants on radical length. Although this rate is generally considered to be diffusion-controlled, the experiments of Sustmann et al.[11b] have shown that the value of $2k_t$ for radicals as similar as the 2-cyano-2-propyl radical and the 1-cyanoallyl radical can differ by factors of 1.5−2. Similar differences in reactivity were observed for the cis and trans butenyl radicals.[11i] The square root of these differences (note eqs 10 and 32) could lead to variations of as much as 20−40%. It is likely that the termination of free radicals is subject not only to viscosity but also to the formation of weak complexes with solvents or other species which are stable enough to affect the rate of termination.[25] More accurate kinetic measurements will require termination rate constants of greater accuracy than those obtained according to the well-known Smoluchowski equation.

The Penultimate Unit Effect. It would be informative to use cobalt-catalyzed reactions in the investigation of copolymerizations as well as the homopolymerizations discussed here. For example, this approach should allow one to study the penultimate unit effect in a free-radical polymerization.[26] The penultimate effect has been shown to play a role in copolymerizations either by distortion of conformational motions in the transition state or through formation of complexes with a free-radical center. We believe that it is also possible that the second unit from the end of the growing chain (penpenultimate unit) can stabilize a radical, in the manner shown in Scheme 5.

Stabilization of radical centers by formation of cyclic acceptor/donor complexes was proposed by Barson and Ensor.[27] These structures were necessary to explain the increase in chain transfer constant for CBr_4 with the increasing degree of polymerization of the growing polyMA radical. It was felt that the complex would have a lower activation energy for chain transfer.[28]

Scheme 6

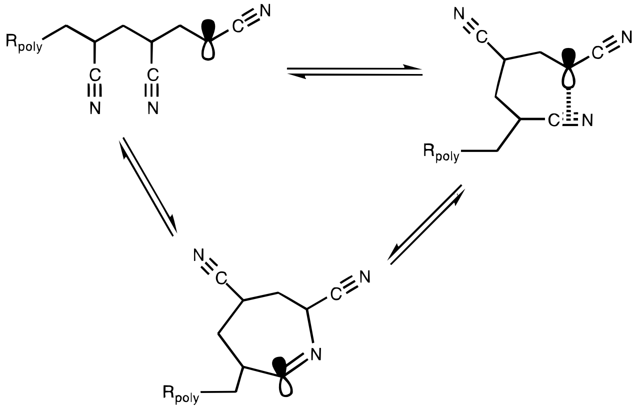
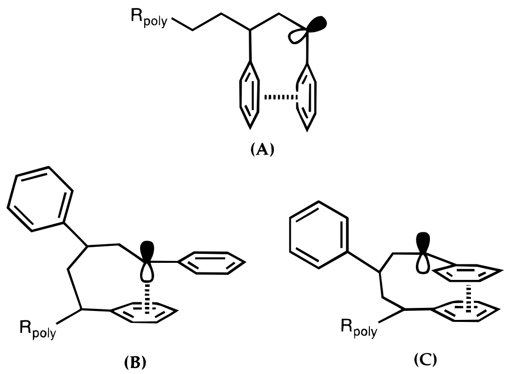


Chart 1



In the cases of styrene and acrylonitrile, the unit second to the end monomer is more likely to interact with the radical center than the penultimate unit due to steric restrictions like those shown in Scheme 6.

Aromatic rings are known to stabilize free radicals by forming complexes.[29] Coplanar structures are believed to be important in aromatic solvent complexes with free radicals.[30] The interaction between the phenyls in neighboring units (structure **A** in (Chart 1)) requires either a prior transformation of the planar radical center into a pyramidal one or a significant bond angle distortion. Alternatively, the interaction between the radical center and the third phenyl (structure **B**) or 1−3 phenyl substituents (structure **C**) with both phenyl substituents and the radical-bearing carbon laying in parallel planes requires little if any change in the conformation of the radical species.

Conclusions

1. Propagation during chain transfer catalysis occurs by a conventional free-radical mechanism. There is no indication of any contribution to propagation through a coordination polymerization mechanism.

2. The relatively clean generation of primary radicals by CTC facilitates the measurement of propagation rate constants for specific radical species. The approach described here is specific to monomers subject to CTC, but the approach could be extended to monomers suitable for metal-mediated living radical polymerizations.

3. For both methyl methacrylate and methacrylonitrile, the propagation rate constants for the primary monomer radicals with DP = 1 are approximately 20 times greater than those determined for high polymeric radicals. The propagation rate constants for dimer radicals of MMA are 4−5 times greater than those of high polymer.

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