# Molecular Weight Distribution of Living Polymerization Involving Chain-Transfer Agents: Computational Results, Analytical Solutions, and Experimental Investigations Using Ring-Opening Metathesis Polymerization†

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ABSTRACT: The number-average degree of polymerization and polydispersity index of living polymerization in the presence of chain-transfer agents are calculated numerically and analytically to determine how the molecular weight of the polymer can be regulated. The solutions reveal that un-steady-state polymerization exists in certain cases. The Mayo plot is nearly linear, but (as opposed to a nonliving system) its slope is not equal to $k_{tr}/k_p$ in general (where $k_i$, $k_p$, and $k_{tr}$ are the specific rate constants of initiation, propagation, and chain transfer, respectively), the former differing from the latter by about 0.5−1 order of magnitude when $k_{tr}/k_p = 0.01-1.0$. Plots of the slopes of Mayo plot versus $k_{tr}/k_p$ for different values of $k_p/k_i$ reveal that only when $k_{tr}$ is equal to or greater than $k_p$ by an order of magnitude can the molecular weight be effectively controlled by addition of chain-transfer agent. A sufficient amount of chain-transfer agent is a necessary but not a sufficient condition to ensure monomodal molecular weight distribution. An analytical expression for the number-average degree of polymerization of the dead chains when $k_{tr} < k_p$ has been derived and shows excellent agreement with numerical results. An analytical expression relating the slope of the Mayo plot to $k_{tr}/k_p$ has also been obtained. These equations hold exactly when the concentration of the catalyst is much less than that of the chain-transfer agent. An experimental investigation of the kinetics of ring-opening metathesis polymerization (ROMP) of norbornene by Mo(=CHCMe$_2$Ph)(NAr)(OCMe$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) (**1**) in the presence of neohexene suggests that this ROMP system is adequately described by a relatively simple polymerization scheme. As measured from NMR spectroscopy, the specific rate constants of initiation, propagation, and chain transfer at 22° C are 0.57, 17, and 0.00003 $M^{-1}$ $s^{-1}$, respectively.

## Introduction

Polymers exhibit properties quite different from their constituent monomers. These properties can all be attributed to their chain length and microstructure.[1] It is therefore of great interest to be able to predict the molecular weight distribution as a function of various reagent concentrations and rate parameters characterizing a particular polymerization system.

Living polymerization is one process that allows precise control of the molecular weight of the polymer.[2] Ideally, the number-average degree of polymerization $\bar{X}_n$ is simply the ratio of monomer to catalyst, while the molecular weight distribution is Poisson in character.[3] Another process involves chain-transfer agents in nonliving polymerization systems. The molecular weight of the polymer can be controlled by the amount of chain-transfer agent because $1/\bar{X}_n$ is a linear function of the ratio [chain-transfer agent]/[monomer].[4] Such a plot (Mayo plot) gives a slope equal to $k_{tr}/k_p$, where $k_{tr}$ and $k_p$ are the specific rate constants for chain transfer and propagation, respectively. The intercept is simply the reciprocal of $\bar{X}_n$ when no chain-transfer agents are present.

In this paper, we direct our attention to the molecular weight distribution of a living polymerization when chain-transfer agents are added.[5] In a typical living polymerization, to obtain low molecular weight polymers, a fixed (and usually substantial) amount of catalyst (i.e., initiator) has to be used because of the absence of any termination step or chain-transfer step. The addition of chain-transfer agents to this system stops the growing polymer chain by transferring the active center from the polymer to the chain-transfer agent, thus starting another chain-growth cycle. A molecule of initiator (or catalyst) thus gives rise to several shorter chain polymers, as if several initiator molecules were used in the first place.

The intentional addition of chain-transfer agents instead of using more catalysts to lower the molecular weight of the polymer is desirable for several reasons. First, catalysts used in certain living polymerization (e.g., ring-opening metathesis polymerization) are usually more expensive, more difficult to synthesize, and generate more undesirable byproducts than chain-transfer agents.[6] The cheaper and easier to synthesize chain-transfer agents offer alternatives for making low molecular weight oligomers. Second, chain-transfer agents added in proper amounts to a living system afford regulation of molecular weight distribution—ranging from the narrow Poisson to broad Flory−Schulz distributions (*vide infra*). Third, polymers with functionalized chain ends could be synthesized readily by allowing the transfer of the desired functional group from the chain-transfer agents bearing such group to the growing polymer chain.[7] These type of polymers (telechelic polymers) cannot be made in a mixed one-batch process through conventional living polymerization because the growing end of the polymer will not contain the desired functional group, unless the chain was end-capped by such a group *at the end of the reaction*.

To our knowledge, the prediction of the chain length and the polydispersity index of living systems with

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chain-transfer agents has not been dealt with adequately before. Most schemes in the literature involve the presence of termination steps (disproportionation or combination) in addition to the usual initiation, propagation, and chain-transfer steps.[8] Such schemes have already been studied intensively, and chain-length dependence of the termination rate constant still remains an area of active investigation.[8]

In this paper, we report the computational results of molecular weight and its distribution for a living system when chain-transfer agents are added deliberately. We examine the validity of the steady-state approximation (constancy of the propagating species) to obtain the distribution of *low molecular weight* oligomers in *living* systems. The significance of the slope of the Mayo plot for a *living* polymerization is re-evaluated because the slope has been taken for granted to be equal to $k_{tr}/k_p$.[7d,7e] Pre-steady-state and post-steady-state behaviors of the reaction are examined as well. Furthermore, the kinetic parameters for a living system are measured experimentally, and the molecular weights obtained experimentally are compared with those obtained by computation.

## Prior Works

Here we briefly examine selected analytical and numerical approaches on molecular weight distributions.

When dealing with *nonliving* systems, the theoretical molecular weight distribution characterizing a particular polymerization scheme is usually obtained through a "kinetic" approach. A kinetic approach involves solving a set of differential equations having rate constants as parameters.[9]

One common approach expresses the rate of change of concentration of each propagating species as functions of the concentration of the propagating species of equal or shorter lengths. These equations may be solved successively for increasingly longer chains by a number of methods (e.g., Laplace transform).[10] Moreover, since the equation governing the consumption of active species of particular chain length depends on the concentration of the active species with length one unit less than that of the former, a difference equation is obtained. Through recursion, the distribution function is obtained as functions of the initial reactant concentrations.

An alternative method rewrites the above steps in terms of various moments of the distribution. Knowledge of all moments is equivalent to knowing the concentration of each species.[11] Tompa elegantly illustrates this concept and that of generating functions to obtain the solution *in the case of high molecular weight polymer* in a variety of polymerization schemes by expressing the distribution as an expansion into Laguerre polynomials.[12]

For certain chain-growth polymerization schemes, it is more advantageous to rewrite the former equations into partial differential equations where the concentrations of the various active species are expressed as functions of the extent of reaction. This approach was used by Saito *et al.* to calculate the number of branch points in chains of specified length in the case of branched polymers.[13]

With regard to *living* polymerization, the case where the monomer itself acts as a chain-transfer agent has been the scope of several investigations.[14,15] Kyner, Radok, and Wales solved this problem by using a modified time variable (introduced by Ginell and Simha) to linearize the systems of differential equations.[14] The molecular weight distribution has the character of a damped wave. As expected, the distribution reduces to the Gold distribution (i.e., modified Poisson distribution) when the monomer cannot act as a chain-transfer agent.[16]

Largo-Cabrerizo and Guzman dealt with the nature of the molecular weight distribution for living polymerization when chain-transfer agents are added deliberately.[17] Because of the additional degree of freedom introduced by using a chain-transfer agent that is not the monomer itself, their solution imposes additional constraints on the system (e.g., the constancy of the monomer concentration and/or chain-transfer agent throughout the reaction; fast initiation; $k_p > k_{tr}$). We are interested in a general solution that can be applied to any given values of rate constants or reactant concentrations.

Cases where the systems have instantaneous initiation or complete initiation have been investigated (especially in the case where the monomer is capable of acting as a chain-transfer agent itself), but the expression for the number-average degree of polymerization is not suitable when the degree of conversion is high.[18]

## Formulation of the Problem

Let CAT, MON, and CTA be the concentrations of catalyst, monomer, and chain-transfer agent, respectively, at time 0, while $W_0$, $M$, $P_0$ are the concentrations of catalyst, monomer, and chain-transfer agent at time $t$. $W_n$ and $P_n$ are the concentration of active and dead polymer chains containing $n$ units of monomer, respectively, at time $t$. $k_i$, $k_p$, and $k_{tr}$ are specific rate constants for initiation, propagation, and chain transfer.[19a]

The polymerization scheme is as follows:

$$W_0 + M \xrightarrow{k_i} W_1$$

$$W_n + M \xrightarrow{k_p} W_{n+1}, \quad n \geq 1$$

$$W_n + P_0 \xrightarrow{k_{tr}} W_0 + P_n, \quad n \geq 1$$

In this scheme, the initiating species $W_0$ produced by the reaction of the chain-transfer agent $P_0$ with the active chain $W_n$ has the same reactivity as the original catalyst $W_0$. This is intentionally done to illustrate the important feature of the system.[19b]

The following kinetic equations describe the above process:

$$dM/dt = -k_i M W_0 - k_p M \sum_{n=1}^{\infty} W_n \tag{1}$$

$$dW_0/dt = -k_i M W_0 + k_{tr} P_0 \sum_{n=1}^{\infty} W_n \tag{2}$$

$$dW_1/dt = k_i M W_0 - k_p M W_1 - k_{tr} P_0 W_1 \tag{3}$$

$$dW_n/d^*t = -k_p M W_n + k_p M W_{n-1} - k_{tr} P_0 W_n, \quad n \geq 2 \tag{4}$$

$$dP_0/dt = -k_{tr}P_0\sum_{n=1}^{\infty}W_n \quad (5)$$

$$dP_n/dt = k_{tr}P_0W_n, \qquad n \geq 1 \quad (6)$$

Using the conservation laws

$$\mathrm{MON} = M + \sum_{n=0}^{\infty}(nW_n) + \sum_{n=0}^{\infty}(nP_n)$$

$$\mathrm{CAT} = \sum_{n=0}^{\infty}W_n$$

$$\mathrm{CTA} = \sum_{n=0}^{\infty}P_n$$

the above equations can be transformed into

$$dM/dt = (k_p - k_i)MW_0 - (k_p\mathrm{CAT})M \quad (7)$$

$$dW_0/dt = (k_{tr}\mathrm{CAT})P_0 - k_iMW_0 - k_{tr}P_0W_0 \quad (8)$$

$$dP_0/dt = k_{tr}W_0P_0 - (k_{tr}\mathrm{CAT})P_0 \quad (9)$$

$$dA/dt = -k_{tr}P_0A + (k_p\mathrm{CAT})M + (k_i - k_p)MW_0 \quad (10)$$

$$dD/dt = k_{tr}P_0A \quad (11)$$

$$dB/dt = -k_{tr}P_0B + k_pM(\mathrm{CAT} + 2A - W_0) + k_iMW_0 \quad (12)$$

$$dF/dt = k_{tr}P_0B \quad (13)$$

where

$$A = \sum_{n=1}^{\infty}(nW_n) \qquad B = \sum_{n=1}^{\infty}(n^2W_n)$$

$$D = \sum_{n=1}^{\infty}(nP_n) \qquad F = \sum_{n=1}^{\infty}(n^2P_n)$$

The number-average degrees of polymerization ($\bar{X}_n$) of the dead and active chains are thus given by

$$\bar{X}_{n\mathrm{dead}} = D/(\mathrm{CTA} - P_0) \qquad \bar{X}_{n\mathrm{active}} = A/(\mathrm{CAT} - W_0) \quad (14)$$

while the polydispersity indices (PDI) of the dead and active chains are

$$\mathrm{PDI}_{\mathrm{dead}} = [F(\mathrm{CTA} - P_0)]/D^2 \qquad \mathrm{PDI}_{\mathrm{active}} = [B(\mathrm{CAT} - W_0)]/A^2 \quad (15)$$

## Computational Methods

The calculations of the differential equations have been performed on Sun SPARCserver 670MPs, using software Mathematica v2.0 (Wolfram Research Inc.). The temporal evolution of the quantities $M$, $W_0$, $P_0$, $\bar{X}_n$, and PDI has been followed. Unless noted otherwise, the resultant values $\bar{X}_n$ and PDI are those for which the percent conversion of monomer is practically complete (unreacted monomer $<10^{-5}$%).

A wide range of magnitudes of rates of initiation, propagation, and chain transfer has been examined. In particular, the specific rates of initiation and propagation range from 100 to 0.01, while those for chain transfer range from 5 to 0.0005. Generally, the concentration of monomer used is from 100 to 1000 times that of the catalyst. The ratio of chain-transfer agent to catalyst has been varied from 2 to 500. Only the relative concentrations of catalyst:monomer:chain-transfer agent and relative values $k_i$:$k_p$:$k_{tr}$ are needed in the calculations (i.e., every quantity can be scaled).

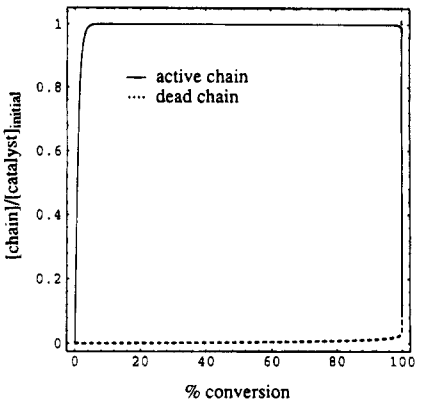


**Figure 1.** Variation of the number of active and dead chains with conversion—poor chain-transfer agent case. $k_i$:$k_p$:$k_{tr}$ = 125:100:0.05. Concentration of catalyst:monomer:chain-transfer agent = 1:100:10.

## Computational Results and Discussion

We first examine the general features of the polymerization for various rate parameters with the intent of gaining insight to how the molecular weight of the polymer can be controlled by varying the chain-transfer agent to monomer ratio. Note that $\bar{X}_n$ is not simply [monomer]/([chain-transfer agent] + catalyst]).

**Cases where $k_{tr} = 0$ or $k_{tr} \ll k_p$.** To check the validity of the numerical approach, we begin by reproducing the results obtained previously from exact mathematical solutions in cases when no chain transfer can occur.[3c,16] When $k_i = k_p$, and in the absence of any chain transfer, $\bar{X}_n$ varies linearly with conversion of the monomer (i.e., extent of reaction). Similarly, the distribution of the molecular weight is Poisson. As expected, when $k_i \neq k_p$, the $\bar{X}_n$ and PDI follow exactly that obtained by Gold.[16a,20]

When the system is perturbed by the addition of a poor chain-transfer agent ($k_{tr} \ll k_p$), the amount of dead chains in the first 98% of the reaction is an extremely small fraction of the total number of chains (active + dead) (Figure 1). Moreover, the $\bar{X}_n$ of the dead chains ($\bar{X}_{n\mathrm{dead}}$) is not a linear function of the extent of reaction. Similarly, the PDI of the active chains ($\mathrm{PDI}_{\mathrm{active}}$) follows closely that of a true living polymerization, while that for the dead chains ($\mathrm{PDI}_{\mathrm{dead}}$) is much greater than $\mathrm{PDI}_{\mathrm{active}}$ but slowly decreases monotonically and converges to $\mathrm{PDI}_{\mathrm{active}}$ as the reaction progresses toward completion. These behaviors are observed because a dead chain is produced only when a *poor* chain-transfer agent reacts occasionally with the active growing chain. Thus, the average molecular weight of the dead chains lags behind that of the active chains, and the distribution of the former is broader. For this reaction, the constancy of the number of propagating species over most of the course of the reaction implies that steady-state approximation can be applied to simplify the eqs 7–13 (*vide infra*) (Figure 1).

**Cases where $k_{tr} \gg k_p$.** Now consider the case where the chain-transfer agent is very efficient ($k_{tr} \gg k_p$). A

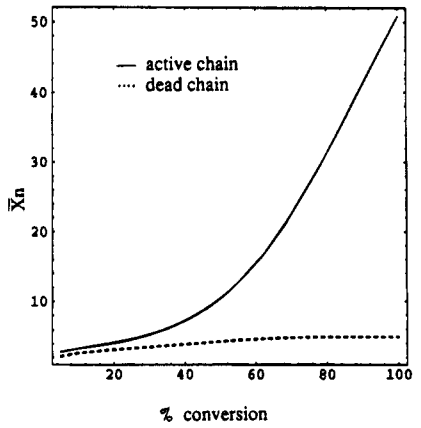


**Figure 2.** Variation of the number-average degree of polymerization with conversion—efficient chain-transfer agent case. $k_i:k_p:k_{tr} = 1.25:1:5$. Concentration of catalyst:monomer:chain-transfer agent = 1:100:10.

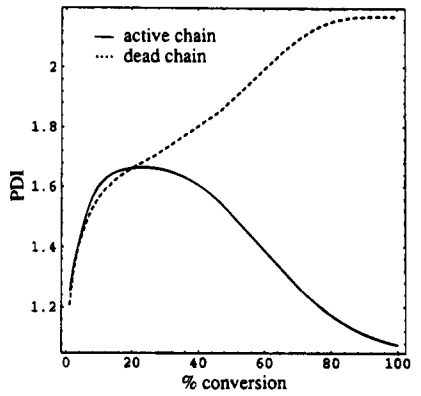


**Figure 3.** Variation of the polydispersity index with conversion—efficient chain-transfer agent case. $k_i:k_p:k_{tr} = 1.25:1:5$. Concentration of catalyst:monomer:chain-transfer agent = 1:100:10.

large percentage of the chain-transfer agent is consumed early in the reaction. This leads initially to dead-chain polymers with short chain lengths (usually between 1 and 10 units long, depending on the concentration of chain-transfer agent). However, once a sufficient amount of chain-transfer agent is depleted, the active chains can only react with the remaining large amount of monomers. The polymerization starts to behave like a true living polymerization (i.e., no chain transfer) and results in active chains with huge chain lengths (Figure 2). This behavior is also apparent in the PDI of the system (Figure 3). Initially, the distribution of the active chains starts to broaden immediately due to rapid chain transfer. At 40% conversion, when most of the chain-transfer agent has been consumed (less than 15% of chain-transfer agent left), the $PDI_{active}$ starts to decrease toward that of a living system (i.e., unity). The polymerization system thus contains large numbers of short oligomers (5 units long) with broad molecular weight dispersion ($PDI_{dead}$ = 2.17) together with a small number of polymers with long chain lengths (50 units long) with narrow dispersion ($PDI_{active}$ = 1.07). Since a significant fraction of the monomers end up as part of the active chains, *a large $k_{tr}$ ($\gg k_p$) does not lead to an efficient yield of short-chain polymers (oligomers).*[21]

**Cases where $k_{tr}$ Is within an Order of Magnitude from $k_p$.** Thus, it is only when $k_{tr}$ is *nearly* of the same order of magnitude as $k_p$ (i.e., within 1 order of magnitude) that the possibility exists for one to control the molecular weight of the polymer. As an example, when

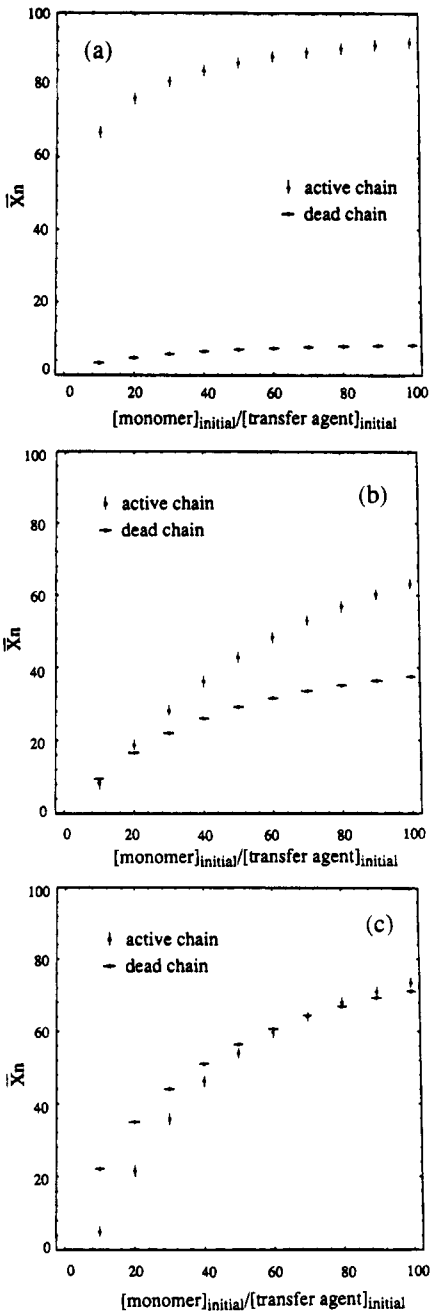


**Figure 4.** Effect of different initial monomer:chain-transfer agent ratio on the number-average degree of polymerization at the end of the reaction. Concentration of catalyst:monomer = 1:100. The concentration of the chain-transfer agent is varied with respect to the monomer accordingly. $k_i:k_p:k_{tr}$ = (a) 1:1:10, (b) 1:1:1, or (c) 1:1:0.1.

$k_{tr}$ is exactly equal to $k_p$, the $\bar{X}_n$ (and also the PDI) values of the active and dead chains are virtually identical at the reaction (see supplementary material).

Figure 4 shows how $\bar{X}_n$ varies with the ratio [monomer]/[chain-transfer agent] when $k_{tr}$ is within 1 order of magnitude from $k_p$ and the reaction is complete. We define the ability to control molecular weight to be as follows: First, the desired chain length is easily achieved by varying the initial monomer concentration to chain-transfer agent ratio. Second, the molecular weight distribution (or polydispersity) should be monomodal. Third, the yield of the reaction should be high. For telechelic polymer synthesis, the last condition implies that most of the monomers should end up as part of the dead chains, formed from active chains end-capped

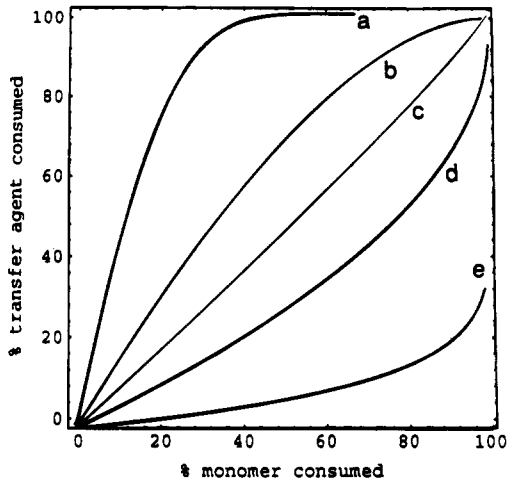


**Figure 5.** Percent chain-transfer agent consumed versus percent monomer consumed when $k_i = k_p = 1$, and $k_{tr}$ = (a) 10, (b) 2, (c) 1, (d) 0.5, or (e) 0.1. Concentration of catalyst: monomer:chain-transfer agent = 1:100:10.

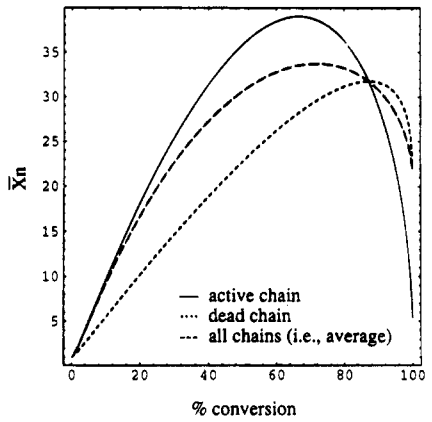


**Figure 6.** Variation of the number-average degree of polymerization with conversion. $k_i:k_p:k_{tr}$ = 1:1:0.1. Concentration of catalyst:monomer:chain-transfer agent = 1:100:10.

during the reaction by chain-transfer agent bearing functional groups.[22]

When $k_{tr} = k_p$, a linear relationship exists between the amount of chain-transfer agent consumed and that of monomer (Figure 5). In spite of this, if insufficient chain-transfer agents are added, the polydispersity remains bimodal (e.g., MON/CTA = 100, a non-negligible portion of the chains are 63 monomer units in length while a certain portion is 38 monomer units in length) (Figure 4b). *Thus, a necessary condition that the molecular weight be controllable is that there should be enough chain-transfer agents in the system.*

When $k_{tr} = 0.1k_p$, two regions arise depending on whether there is an excess of chain-transfer agent or not (Figure 4c). When [monomer]/[chain-transfer agent] < 70, not all chain-transfer agents are consumed at the end of the reaction. Though the distribution seems bimodal, the actual amount of active chains at high conversion is extremely small and negligible (see supplementary material). Thus, at the end of the reaction, the number-average degree of polymerization of all chains $\bar{X}_{n\text{all}}$ (i.e., regardless of whether the chain is active or dead) is weighted toward $\bar{X}_{n\text{dead}}$ (Figure 6). The $\text{PDI}_{\text{dead}}$ for the first 90% of the reaction is about 1.5 and rises steeply to 2.2 only in the last 4% of the reaction (Figure 7). For this particular set of rate constants, the molecular weight can therebore be controlled in this region.

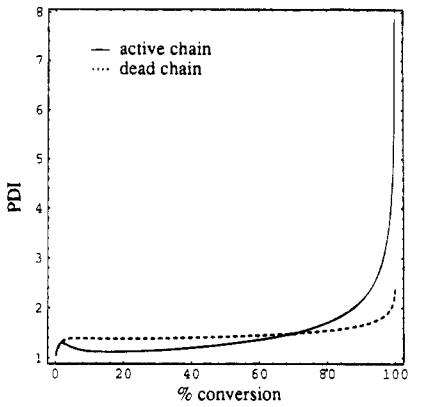


**Figure 7.** Variation of the polydispersity index with conversion. $k_i:k_p:k_{tr}$ = 1:1:0.1. Concentration of catalyst:monomer: chain-transfer agent = 1:100:10.

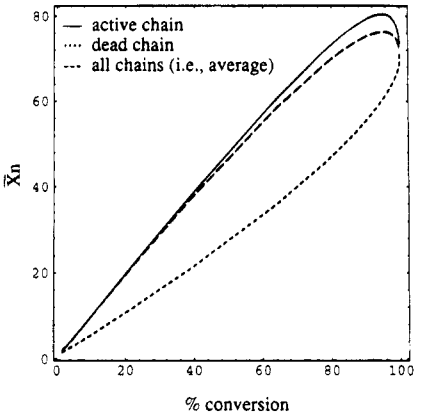


**Figure 8.** Variation of the number-average degree of polymerization with conversion. $k_i:k_p:k_{tr}$ = 1:1:0.1. Concentration of catalyst:monomer:chain-transfer agent = 1:100:1.

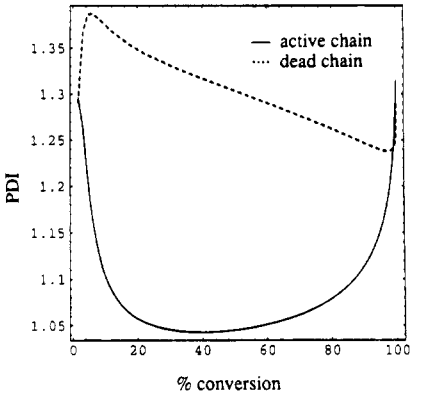


**Figure 9.** Variation of the polydispersity index with conversion. $k_i:k_p:k_{tr}$ = 1:1:0.1. Concentration of catalyst:monomer: chain-transfer agent = 1:100:1.

When [monomer]/[chain-transfer agent] > 70, the plot of percent chain-transfer agent consumed versus percent monomer consumed still has the same form as curve e in Figure 5. Although only about 20% of the chain-transfer agent has reacted at 90% conversion of the monomer, both are used up eventually.[22] Under this condition, 29% of the monomer ends up as part of the active chains. Unlike the preceding case, $\bar{X}_{n\text{all}}$ is weighted toward $\bar{X}_{n\text{active}}$ throughout most of the reaction (Figure 8). Nevertheless, the active and dead chains each have values of $\bar{X}_n$ that ultimately *converge to the same value* while their PDIs remain below 1.4 (Figure 9). Therefore, *complete consumption of both chain-transfer agent and monomer plus a monomodal molecular weight*

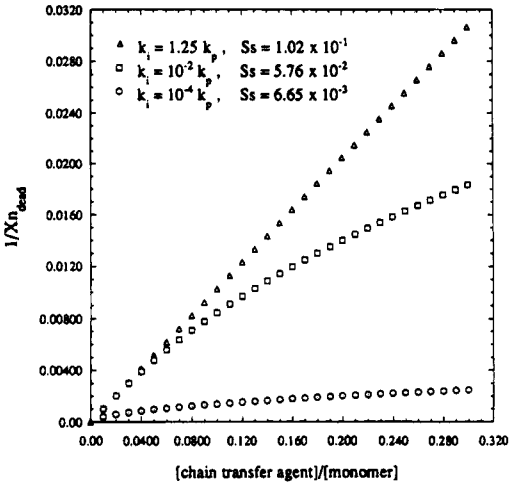


**Figure 10.** Mayo plot. $k_{tr}/k_p$ is set at $5.0 \times 10^{-4}$. Concentration of catalyst:chain-transfer agent = 1:10. Concentration of monomer is varied accordingly. The slope Ss varies with initiation rate and is not equal to $k_{tr}/k_p$. The slope Ss is derived from a least-squares fit of $1/\bar{X}_{nall}$ with $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$.

*distribution does not guarantee the total absence of active chains*. Hence, if both chain-transfer agent and monomer are totally consumed, a *necessary but not sufficient* condition for the controlled synthesis of *telechelic* polymer is the presence of enough chain-transfer agents to end-cap the remaining active chains near the end of the reaction.

**Mayo Plot and $k_{tr}/k_p$.** We now examine the features of the Mayo plot to determine whether its slope has the same significance for a living system (with deliberate addition of chain-transfer agent) as compared with that of a nonliving system, as certain studies have employed its slope as a measure of $k_{tr}/k_p$ regardless of whether the polymerization is living or not.[4,23] A correlation of greater than 0.98 is always obtained in this polymerization scheme when $1/\bar{X}_n$ is plotted against $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$ (see explanation under Analytical Results and Discussion).[24] However, in contrast to *nonliving* polymerization (i.e., presence of termination not arising from chain transfer), *the slope Ss of the Mayo plot for a living polymerization may differ from $k_{tr}/k_p$ by orders of magnitude*[4,23] (Figure 10). This arises since the Mayo equation does not take into account the concentration of the catalyst, which in a true living polymerization controls the $\bar{X}_n$ as well. The slope Ss also changes with $k_i$ and is not related to the ratio $k_{tr}/k_p$ in a simple manner. As expected, as the specific rate of initiation increases relative to propagation, $\bar{X}_n$ decreases and therefore the slope Ss increases.

Before a graphical relationship between $k_{tr}/k_p$ and the slope (*vide infra*) is derived, it should be noted that even when the ratio $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$ remains a constant, the degree of polymerization $\bar{X}_{ndead}$ at the end of the reaction may be dependent on the amount of catalyst used in the polymerization (Figure 11). This results implies that for a living polymerization the slope Ss may depend on which reagent (chain-transfer agent or monomer) is varied when the Mayo plot is constructed. To further illustrate, the Mayo plot that is obtained by varying the concentration of chain-transfer agent while keeping the ratio $[\text{monomer}]_{initial}/[\text{catalyst}]_{initial}$ constant is dramatically different from that obtained when it is the concentration of monomer that is varied but then ratio $[\text{chain-transfer agent}]_{initial}/[\text{catalyst}]_{initial}$ is kept constant (Figure 12). Note that

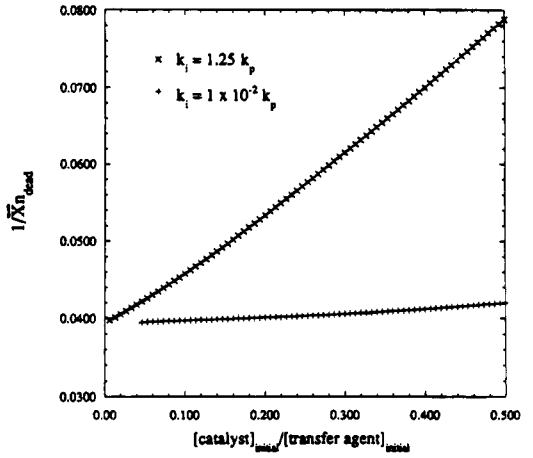


**Figure 11.** Dependence of number-average degree of polymerization on concentration of catalyst. [Chain-transfer agent]/[monomer] = 0.10 and $k_{tr}/k_p = 0.10$. [Catalyst] varies from 0.01333 to 0.5 times [chain-transfer agent].

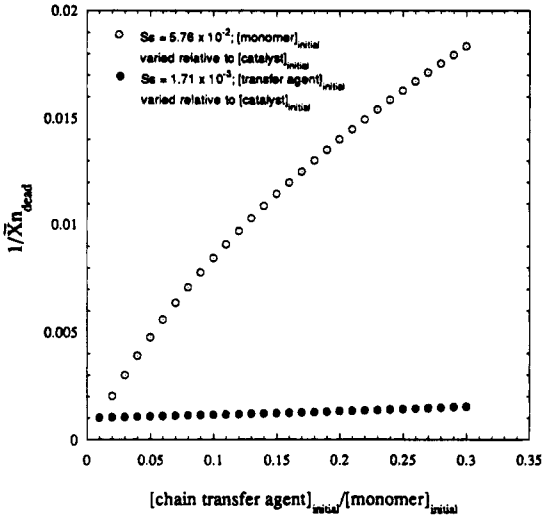


**Figure 12.** Comparison of the slopes of Mayo plots for two different reaction conditions: (⊙) [monomer] varied relative to [catalyst]; (●) [transfer agent] varied relative to [catalyst]. $k_i:k_p:k_{tr} = 1:100:0.01$. The leftmost data point corresponds to catalyst:monomer:chain-transfer agent = 1:1000:10.

in both cases the value of $\bar{X}_n$ is different for the same values of $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$ by virtue of how the experiment is conducted.

For a given $k_p/k_i$, we next constructed a graphical relationship between Ss and $k_{tr}/k_p$ as a way to obtain $k_{tr}/k_p$ by using the slope from the Mayo plot. The values $k_p/k_i$ can easily be measured experimentally by an independent method.[16a]

When $[\text{chain-transfer agent}]_{initial}/[\text{catalyst}]_{initial}$ is fixed while $[\text{monomer}]_{initial}$ is allowed to vary, the graph shows three well-defined regions (Figure 13). In the rightmost region, the slope Ss converges to 1 (hence log Ss = 0) regardless of the rate of initiation. This behavior is understood by noting that when $k_{tr} \gg k_p$, the expression $\bar{X}_{nall} = (A + D)/[(\text{CAT} - W_0) + (\text{CTA} - P_0)]$ reduces to $\bar{X}_{nall} \approx \text{MON/CTA}$ because $(A + D) = \text{MON}$, $P_0 = 0$, and CAT < CTA. Hence $1/\bar{X}_{nall} \approx \text{CTA/MON}$ and Ss = 1. For the leftmost region, $k_{tr} \ll k_p$; hence, $\bar{X}_n$ reduces to the limiting value given by Gold's paper and the slope Ss is independent of the value $k_{tr}/k_p$.[16a] Therefore, consistent with the conclusion of the preceding section, $k_{tr}/k_p$ can only take a narrow range of values for the system to exhibit effective molecular weight control.

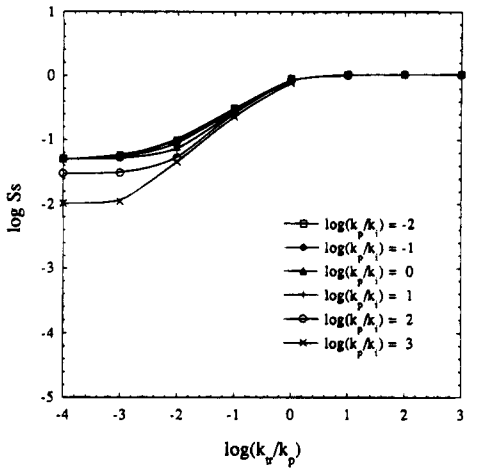


**Figure 13.** Relationship of the slope Ss of Mayo plot to $k_{tr}/k_p$ for different $k_p/k_i$. [Chain-transfer agent]/[catalyst] = 20; [monomer] varies from 2 to 20 times [chain-transfer agent]. The slope Ss is derived from a least-squares fit of $1/\bar{X}_{nall}$ with $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$.

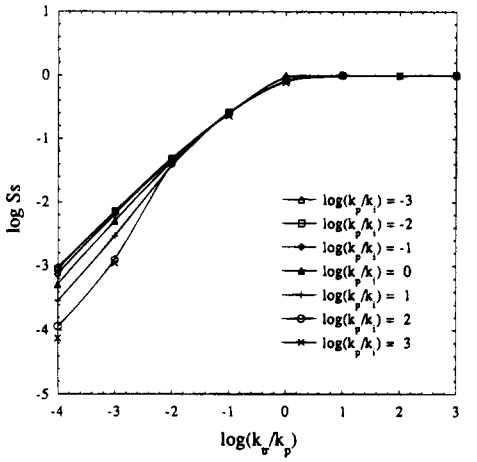


**Figure 14.** Relationship of the slope Ss of Mayo plot to $k_{tr}/k_p$ for different $k_p/k_i$. [Monomer]/[catalyst] = 100; [transfer agent] varies from 2 to 20 times [monomer]. The slope Ss is derived from a least-squares fit of $1/\bar{X}_{nall}$ with $[\text{chain-transfer agent}]_{initial}/[\text{monomer}]_{initial}$.

Similarly, when $[\text{monomer}]_{initial}[\text{catalyst}]_{initial}$ is fixed while $[\text{chain-transfer agent}]_{initial}$ is allowed to vary, the graph also shows three regions of interest (Figure 14). Again, only in the central region where $k_{tr} \sim 0.1k_p$ or $1.0k_p$ does the possibility exist for controlling the molecular weight. The rightmost region shows Ss having a value of unity, regardless of how high $k_{tr}/k_p$ gets. This result showing that Ss is not equal to $k_{tr}/k_p$ might explain the observation that apparent rate constants $k_{tr}/k_p$ of reactive acyclic olefins taken from the Mayo plot are usually lower than the results obtained from telomer ratios.[7e]

## Analytical Results and Discussion

**Steady-State Approximation and Closed-Form Solution.** It is known that in a polymerization scheme consisting only of initiation, propagation, and chain transfer an un-steady-state polymerization results; i.e., the number of active chains is *not* invariant.[14a] Such cases also exist in our scheme (monomer incapable of acting as chain-transfer agent).[25]

Inasmuch as the steady-state assumption greatly simplifies the analytical expression of $\bar{X}_n$ for a great variety of polymerization schemes (living or nonliving), we now impose such an assumption on our system for comparison with the numerical solution obtained above. This assumption is not entirely invalid since certain cases we examined gave steady-state kinetics (e.g., Figure 1).

By definition, steady-state is said to occur when the rate of change of the amount of active chains in solution is much less than the rate of active-chain formation or destruction, i.e.

$$\mathrm{d}\left(\sum_{n=1}^{\infty} W_n\right)/\mathrm{d}t \ll \text{minimum (rate of formation or of destruction of active species)}^{9e} \quad (16)$$

It is important to observe from this definition that $\mathrm{d}(\sum_{n=1}^{\infty} W_n)/\mathrm{d}t \approx 0$ is not a sufficient condition for the existence of steady state.[9e]

In spite of the above conditions, in a nonliving polymerization, it is customarily assumed that

$$\mathrm{d}W_n/\mathrm{d}t = 0 \text{ for } n \geq 0^{9,15} \quad (17)$$

In a living polymerization, this strong form of the steady-state approximation does not lead to the correct expression for $\bar{X}_n$.[26] However, we have observed (through numerical calculation) that the weaker form of the steady-state approximation

$$\mathrm{d}W_0/\mathrm{d}t = 0 \quad (18)$$

occurs frequently when $k_{tr} < k_p$. Thus, eq 2 becomes

$$\sum_{n=1}^{\infty} W_n = (k_i W_0 M)/(k_{tr} P_0) \quad (19)$$

Substituting eq 19 into the quotient of eqs 1 and 5 gives

$$\partial M/\partial P_0 = 1 + (k_p/k_{tr})(M/P_0) \quad (20)$$

Therefore

$$M = \frac{P_0}{1 - \frac{k_p}{k_{tr}}} + \left(\mathrm{MON} - \frac{\mathrm{CTA}}{1 - \frac{k_p}{k_{tr}}}\right)\left(\frac{P_0}{\mathrm{CTA}}\right)^{k_p/k_{tr}} \quad (21)$$

*Consider the case when $k_{tr} < k_p$ and a sufficient amount of chain-transfer agents is used in the reaction.* At the end of the reaction, $M = 0$. The amount of chain-transfer agent left is

$$P_0 = \mathrm{CTA}\left[1 + \left(\frac{k_p}{k_{tr}} - 1\right)\left(\frac{\mathrm{MON}}{\mathrm{CTA}}\right)\right]^{-1/(k_p/k_{tr} - 1)} \quad (22)$$

Since no active chains are left, the equation $\bar{X}_{ndead} = \mathrm{MON}/(\mathrm{CTA} - P_0)$ becomes

$$\bar{X}_{nall} = \bar{X}_{ndead} = \frac{\mathrm{MON}}{\mathrm{CTA}} \frac{1}{1 - \left[1 + \left(\frac{k_p}{k_{tr}} - 1\right)\left(\frac{\mathrm{MON}}{\mathrm{CTA}}\right)\right]^{-1/(k_p/k_{tr} - 1)}} \quad (23)$$

Figure 15 shows an excellent agreement between the analytical solution for $\bar{X}_{ndead}$ shown above and that obtained by numerical approach discussed in the previous section. The expression for $\bar{X}_n$ in eq 23 is independent of the rate of initiation, the catalyst concentration, and the manner by which the experiment is conducted (*cf.* previous section). This results from the requirement that a sufficient amount of chain-transfer agent be present in the system, *which implies an initial condition of* $[\text{catalyst}]_{intiat} \ll [\text{chain-transfer agent}]_{initial}$.[27a]

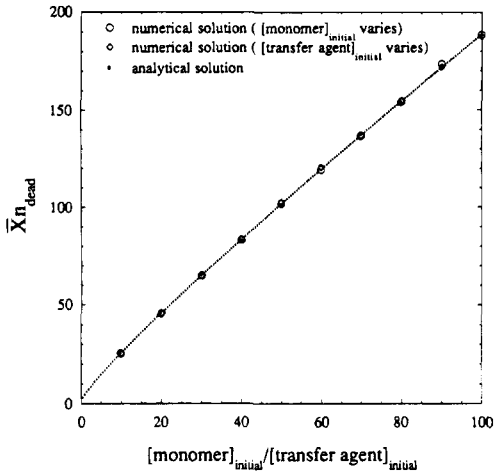


**Figure 15.** Comparison of analytical and numerical solutions for $\bar{X}_n$ at different $[monomer]_{initial}/[transfer\ agent]_{initial}$ ratios. $k_i:k_p:k_{tr} = 1:1:0.1$. For the first numerical solution, $[transfer\ agent]_{initial}/[catalyst]_{initial} = 2 \times 10^3$ as $[monomer]_{initial}$ is varied; for the second numerical solution, $[monomer]_{initial}/[catalyst]_{initial} = 2 \times 10^4$ as $[transfer\ agent]_{initial}$ is varied.

Equation 23 predicts that when the above initial conditions hold, the Mayo plot should be nearly linear with a slope $d(1/\bar{X}_n)/d(\mathrm{CTA/MON})$ given by[27b]

$$S_c = \frac{d\left(\frac{1}{\bar{X}_n}\right)}{d\left(\frac{\mathrm{CTA}}{\mathrm{MON}}\right)} = 1 - \left(1 + \frac{1}{\frac{\mathrm{CTA}}{\mathrm{MON}} + \frac{k_p}{k_{tr}} - 1}\right)\left(1 + \frac{\frac{k_p}{k_{tr}} - 1}{\frac{\mathrm{CTA}}{\mathrm{MON}}}\right)^{-1(k_p/k_{tr} - 1)} \quad (24)$$

The plot of eq 24 is in close agreement with Figure 14, despite the fact that in Figure 14 $[catalyst]_{initial}$ is within an order of magnitude of $[chain\text{-}transfer\ agent]_{initial}$ (see supplementary material). It can be shown that the slope $S_c$ is practically independent of the ratio [monomer]/[chain-transfer agent] when the ratio is greater than 10. Thus, the value of $k_{tr}/k_p$ can be determined from a construction of Mayo plot and the use of $S_c$ (Figure 16). It may also be shown analytically that $S_c$ is independent of the quantity CTA/MON when $k_{tr}/k_p$ approaches 0.

## Experimental Section

**General Methods.** All manipulations of air- and/or moisture-sensitive compounds were carried out under argon using standard Schlenk and vacuum line techniques. Argon was purified by passing through columns of activated BASF RS-11 (Chemalog) oxygen scavenger and Linde 4A molecular sieves. Solids were weighed in a drybox equipped with a MO-40-1 purification train. Toluene and mesitylene were distilled from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves; norbornene was stirred with sodium at 60 °C and distilled into a small Schlenk flask and degassed; neohexane (Aldrich) was distilled from calcium hydride under vacuum into a medium Schlenk flask and subsequently freeze–pump–thaw degassed. Prior to use, neohexane was passed through a small column of alumina (activated) inside the drybox. $Mo(=CHCMe_2Ph)(NAr)(OCMe_3)_2$ (Ar = 2,6-diisopropylphenyl) (**1**) (Strem Chemicals) was used directly without further purification.

$k_i$ and $k_{tr}$ were measured via $^1H$ NMR on a JEOL GX-400 (399.65 MHz $^1H$), while $k_p$ was measured on a GE NMR instrument QE-Plus-300 (300.19 MHz $^1H$) and on a Hewlett-Packard 5890 Series II gas chromatograph (0.25 $\mu$m Alltech

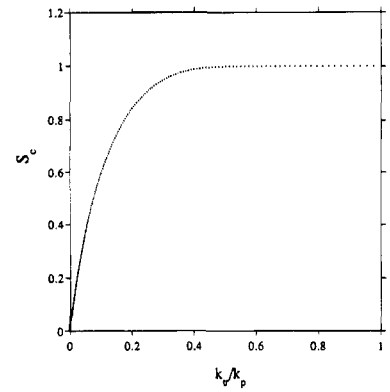


**Figure 16.** Relationship of $S_c$ (as determined from eq 24) to $k_{tr}/k_p$. The plot remained the same whether [monomer]/[chain-transfer agent] was 1000, 100, or 10.[27]

OV101 column). The molecular weights of the polymers were measured on a Waters 150-C ALC/GPC [gel permeation chromatography column (Waters Ultrastyragel $10^5$, $10^4$, $10^3$, 500 Å; toluene), relative to polystyrene standard].

**Determination of Ratio $k_p/k_i$.** Norbornene (32.9 mg) was dissolved in 1.6 mL of toluene-$d_8$ mixed with 0.15 $\mu$L of mesitylene to make a 1.620 mL solution; 400 $\mu$L of this solution (0.0864 mmol in norbornene) was placed in an NMR tube at 22 °C, and the NMR spectrum was taken to ensure that no polymer had been formed. In another vial, 31.9 mg of **1** was dissolved in 950 $\mu$L of toluene-$d_8$; 300 $\mu$L of this solution (0.01845 mmol in **1**) was injected into the NMR tube. The tube was shaken vigorously and dropped into the NMR probe at 22 °C. After 30 min, when the polymerization was complete, the α-H of the initial carbene **1** and that of the propagating carbene ($\delta$ = 11.28 and 11.52, respectively) were integrated relative to the mesitylene standard, respectively. For this trial, the ratio of remaining catalyst to total catalyst was 0.574. Hence $k_p/k_i$ = 33.0. From the same stock solution, the same volume of aliquot was withdrawn for a second trial to give $k_p/k_i$ = 28.0. The stock solution was not used again for further $k_p/k_i$ measurements. The two NMR tubes were saved for subsequent measurements of $k_{tr}$. New stock solutions were prepared using 17 mg of norbornene in 200 $\mu$L of toluene and 5.1 and 6.1 mg of **1** weighted into separate NMR tubes. The results of similar measurements from different preparations gave $k_p/k_i$ = 35.2, 27.5, 35.6, 29.5, and 20.7. Except for the last value, which was obtained through autointegration from the 300 MHz NMR spectrometer, all other values were integrated manually via the 400 MHz NMR spectrometer. Discarding the last value, an average value of 30 was obtained.

**Determination of $k_{tr}$.** To each of the two NMR tubes in the preceding section was injected 20 $\mu$L of neohexene, and the tubes were shaken vigorously. The disappearance of propagating carbene signal at $\delta$ = 11.52 and the appearance of new carbene signal at $\delta$ = 11.23 were monitored about every 6 h for 1.5 days. From the second-order kinetic plot, the calculated $k_{tr}$ values were 0.0090, 0.073, 0.170, and 0.085. The average 0.105 ± 0.04 $M^{-1}\ h^{-1}$ was obtained (Figure 19).

**Determination of $k_p$. a. By NMR.** $k_p$ at 22 °C was too large to be measured directly by NMR spectroscopy. An Eyring plot was constructed instead. Norbornene (49.1 mg) with 0.5 $\mu$L of mesitylene was dissolved in 2.50 mL of toluene-$d_8$ to make 2550 $\mu$L of solution; 500 $\mu$L aliquots were injected into four NMR tubes. NMR spectra were then obtained at several temperatures (−10, −19, −30.2 and −46 °C).

**1** (14.3 mg) was dissolved in 1.00 mL of toluene. A 20 $\mu$L aliquot of this catalyst solution was injected into the NMR tube dipped in liquid $N_2$, and then the tube was immediately transferred into the probe already set at the correct temperature. After about a minute, the tube was ejected, shaken once, and then dropped back down into the probe. Data were collected in 2 min intervals for 50 min. The disappearance of the signals corresponding to the olefin protons of the monomer in the NMR spectrum was used to determine $k_p$. The $^1H$ signal of poly(norbornene) was not used due to the chain-length

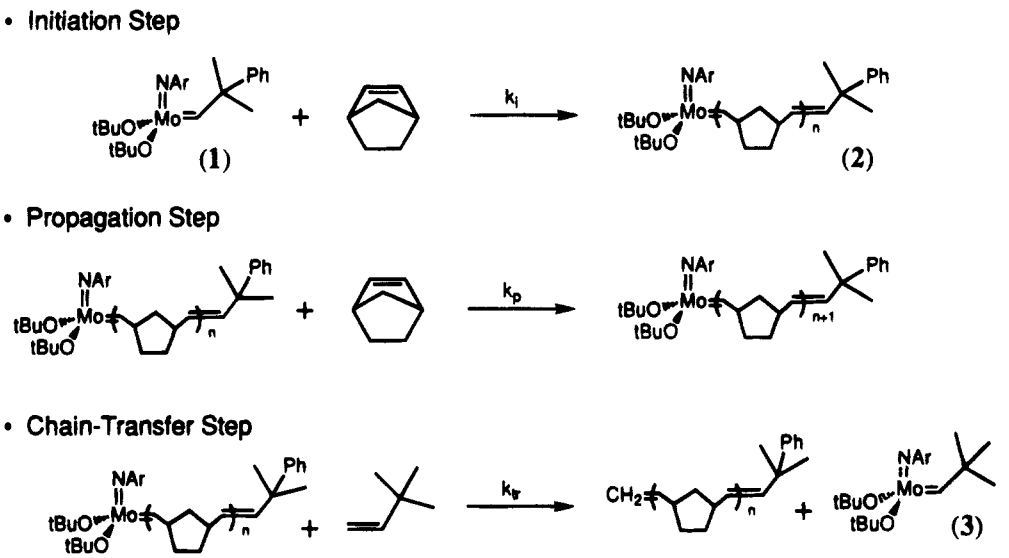


**Figure 17.** Polymerization scheme of norbornene by Mo=(CHCMe$_2$Ph)(NAr)(OCMe$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) in the presence of neohexene in toluene.

dependence of the relaxation rate of the polymer protons. $k_p$ = 17 $M^{-1}$ $s^{-1}$ by extrapolation of the Eyring plot (see Table 2).

**b. By GC.** In the drybox, 38.4 mg (796.6 equiv) of norbornene was dissolved in 5 mL of toluene in a vial containing a spinbar; 5 $\mu$L of mesitylene was added as internal standard. A 100 $\mu$L aliquot of a solution of 5.6 mg of **1** in 2 mL of toluene was withdrawn and added to the norbornene solution above. The solution was stirred rapidly. One drop aliquot (~20 $\mu$L) of this solution was withdrawn every 30 s for the first 5 min and placed in a series of vials containing 2 drops of benzaldehyde (to quench the reaction) and 4 drops of toluene. For the next 15 min, a drop was collected every minute and mixed with the benzaldehyde/toluene solution. At the end of 20 min, the contents of these 25 vials were brought out of the drybox and 4 drops of methanol was added to each vial to precipitate the polymer. The resultant solution was injected into the GC. The integral of norbornene signal relative to mesitylene signal was used in a first-order kinetic plot to obtain the value of $k_p$ of 15 $M^{-1}$ $s^{-1}$. Correlation coefficient = 0.987.

**Measurements of Molecular Weights through Size Exclusion Chromatography.** Norbornene (405.2 mg) was dissolved in 2.50 mL of toluene to make 2.92 mL of solution. To each of five vials (with spinbar) was added 500 $\mu$L of this solution. The remaining solution was placed into vial 6 (for control). Then 10.0, 7.5 5.0, 2.5, 2.5, or 2.5 mL of toluene was added to the six vials, respectively. Then 0, 2.5, 5.0, 7.5, 10.0, or 1.0 mL of neohexene was added to the six vials, respectively. To each of the first five vials was injected 150 $\mu$L of solution of **1** prepared by dissolving 15.7 mg of **1** in 1 mL of toluene. The vials were sealed with a Teflon cap and stirred for 1.5 h at room temperature. All of the solutions remained clear during the time period. The volumes of the solution in the first four vials are the same. After 2 h, 10 $\mu$L of benzaldehyde was injected into the six vials. After stirring for another 20 min, the vials were exposed to air and heated to 60 °C in an oil bath to evaporate off the unreacted neohexene. The solutions were then passed through alumina to remove the dead catalyst and subsequently filtered, diluted, and injected into the GPC column to obtain the molecular weight.

## Experimental Results and Discussion

The living ring-opening metatheses polymerization (ROMP) of norbornene and norbornene-type monomers by **1** are well established by Schrock and co-workers.[6b,28a,d] The reactions of **1** with several acyclic olefins have been extensively investigated.[28b,c] Because the initiating, the propagating, and the chain-transferred metal alkylidene (**1**, **2**, and **3**, respectively) each exist as one rotamer only (anti, and no syn), the system in Figure 17 thus fits the polymerization scheme outlined above (see Formulation of the Problem).[6b,28d,f] **1** and **3** also have the same reactivity because the reactivity of the catalyst is governed primarily by the alkoxide ligands, the steric influence of the isopropyl ligands on the imido group, and the immediate substituent on carbon making up the metal–alkylidene bond.[28] Neohexene ensures that **3** is structurally similar to **1** and ensures reinitiation. Therefore, once the experimental rate constants are known, numerical methods can be used to compute the $\bar{X}_n$ for given concentrations of the reactants.

$$\frac{k_p}{k_i} = \frac{\dfrac{M - \mathrm{MON}}{\mathrm{CAT}} - \dfrac{W_0}{\mathrm{CAT}} + 1}{\ln\dfrac{W_0}{\mathrm{CAT}} - \dfrac{W_0}{\mathrm{CAT}} + 1} \qquad (25)$$

The ratio $k_p/k_i$ as shown in the analytical equation above is very sensitive to the measured value of $W_0$/CAT when the latter approaches unity (Figure 18).[16a] In the absence of neohexene, when [norbornene]$_{initial}$/[**1**]$_{initial}$ is about 5, $k_p/k_i$ = 30 (as determined from the amount of unreacted **1**). As calculated from eq 25, an error of 6% in the NMR integrals for $W_0$ and CAT in this case makes $k_p/k_i$ range from 27 to 33.[29]

When $k_p$ is measured, two observations are made. First, from the value $k_p/k_i$ = 30, 1000 equiv of norbornene is needed so that 99% of the catalyst would have been initiated when 11% of the monomer is consumed—as calculated from eq 25 (Table 1). Since during the reaction the 0.520 mL of toluene solution turns into a gel when 1033 equiv of norbornene is used, to minimize the viscosity dependence of the rates measured, 195.5 equiv of norbornene is used instead. The first 50% of the kinetic data are discarded since, theoretically, less than 99% of catalyst would have initiated (Table 1). Otherwise, a smaller-than-actual $k_p$ value would have been measured.

Second, the value $k_p$ = 17 $M^{-1}$ $s^{-1}$ at 22 °C was obtained by extrapolating the values measured at lower temperatures (Eyring plot) (Table 2). The slight nonlinearity (upward concavity) of the Eyring plot might be the consequence of the formation of metallacycle

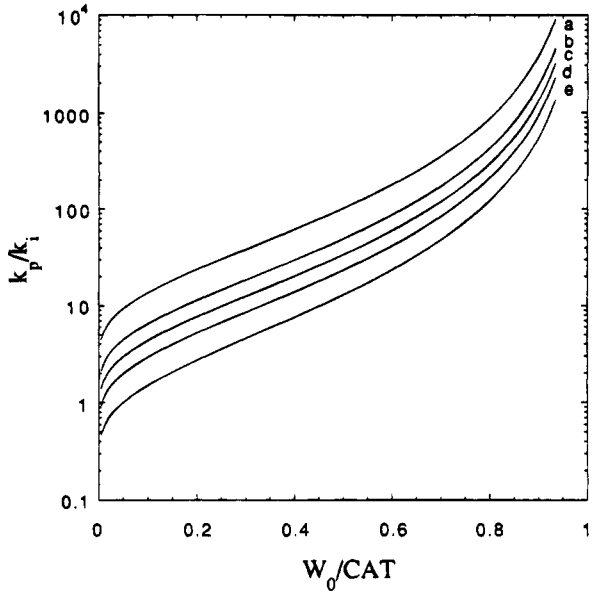


**Figure 18.** Relationship between $k_p/k_i$ and $W_0$/CAT when $[monomer]_{initial}/[catalyst]_{initial}$ is (a) 20, (b) 10, (c) 7, (d) 5, or (e) 3. $W_0$ is concentration of unreacted catalyst at the end of reaction. CAT is initial concentration of catalyst.

**Table 1. Theoretical Percent Catalyst Initiated at Certain Conversion of the Monomer for Particular Starting Ratio of Monomer to Catalyst When $k_p/k_i = 30$**

| MON/CAT | % conversion monomer | % catalyst initiated |
|---|---|---|
| 1000 | 11.0 | 99 |
| 547.2 | 20.0 | 99 |
| 214 | 20.0 | 90 |
| 214 | 51.1 | 99 |
| 195.5 | 56.0 | 99 |

**Table 2. Specific Rates of Propagation for Construction of Eyring Plot[a]**

| temp, °C | $k_p$, $M^{-1}$ $m^{-1}$ | correl coeff | $1/T$, $K^{-1}$ | $\ln(4k_p/T)$, $M^{-1}$ $s^{-1}$ $K^{-1}$ |
|---|---|---|---|---|
| −46 | 30.1 | 0.999 | 0.004405 | −6.116 |
| −30.2 | 64.6 | 0.994 | 0.004119 | −5.418 |
| −19.0 | 123 | 0.998 | 0.003937 | −4.820 |
| −10 | 276 | 0.995 | 0.003802 | −4.045 |

[a] $\Delta H^{\ddagger} = 6.6$ kcal/mol. $\Delta S^{\ddagger} = -15.4$ eu. Correlation coefficient of Eyring plot is 0.98. $k_p$ at 22 °C = $T/M^{-1}$ $s^{-1}$ by extrapolation.

intermediate or olefin complex at low temperatures which can influence the rate of consumption of norbornene.[30]

Using GC, much of the difficulties in measuring $k_p$ through NMR are circumvented. Since the solution is diluted (thus slowing the reaction) and a faster sampling rate is possible (as compared with the NMR), more data points can be collected, allowing the experiment to be conducted at room temperature.[31] $k_p$ is obtained by GC at 22 °C is 15 $M^{-1}$ $s^{-1}$ (correlation coefficient = 0.987), a value comparable to that obtained from NMR. Thus, $k_i$ is 0.57 $M^{-1}$ $s^{-1}$.

To measure $k_{tr}$, the propagating carbene **2** has to be created from initiating carbene **1** (Figure 17). When 4.68 equiv of norbornene is added to **1**, only 42.6% of **1** reacts to form **2**. No more norbornene is added because the $^1H$ NMR signals of the alkylidene proton of the catalysts would be too small to be measured with accuracy. Next, 18.6 equiv (relative to **2**) of neohexene is added. The disappearance of **2** and the appearance of **3** through chain transfer by acyclic metathesis with neohexene are then followed by NMR.

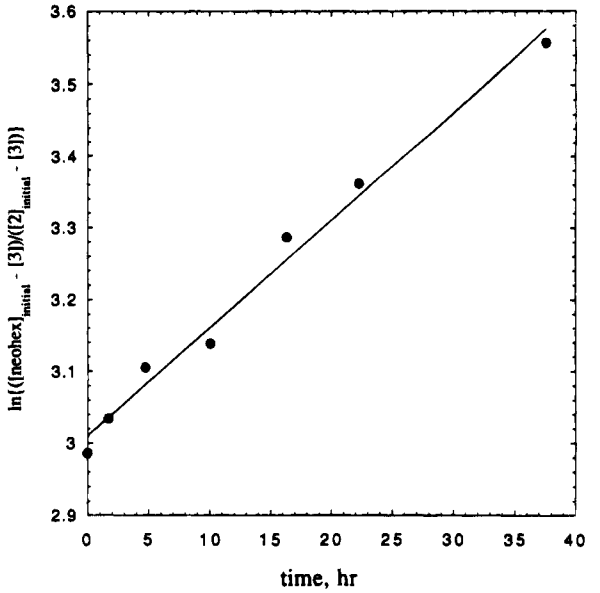


**Figure 19.** Second-order kinetic plot of information of **3** from reaction of **2** with neohexene.

**Table 3. Variation of Number-Average Degree of Polymerization with [Neohexene]/[Norbornene] at 22 °C When [Norbornene]/[1] = 151.7[a]**

| [neohexene]/ [norbornene] | $\bar{M}_n$[b] | $\bar{X}_n$, exptl[c] | PDI, exptl | $\bar{X}_n$, theor[d] | PDI, theor |
|---|---|---|---|---|---|
| 0 | 49 700 | 152 | 1.06 | 152 | 1.04 |
| 26.51 | 47 500 | 145 | 1.05 | 150 | 1.05 |
| 53.03 | 45 500 | 139 | 1.08 | 147 | 1.07 |
| 79.54 | 40 600 | 124 | 1.12 | 145 | 1.08 |
| 106.05 | 41 900 | 128[e] | 1.14[e] | 143 | 1.09 |

[a] The volume of the solutions is kept constant by addition of appropriate of toluene. The last table entry contains about 14% toluene. [b] Relative to polystyrene standard. [c] Factor of 3.5 is used to convert molecular weight referenced to polystyrene to that of polynorbornene.[34] [d] As calculated from substituting the specific rates into the differential equations. [e] For this entry, more toluene is added to increase the volume of solution during polymerization to prevent polymer precipitation.

To rule out the possibility that **3** is formed directly by the acyclic metathesis of **1** with neohexene, 13.9 equiv of neohexene is added to **1** in another NMR tube. After a day, no detectable amount of **3** has formed. After a week, about 5% of **1** has been converted to **3**. The fact that neohexene reacts more rapidly with **2** than with **1** is due to the greater steric crowding at the $\beta$-carbon of **1** (quaternary) than that at **2** (tertiary carbon).[28,32] As expected, **1**− and **3** are stable for at least the duration of the experiment. From the second-order kinetic plots, $k_{tr}$ at 22 °C is $3 \times 10^{-5}$ $M^{-1}$ $s^{-1}$, suggesting that it is a very poor chain-transfer agent (Figure 19).[33] This small value is not unreasonable because in the reaction of **1** and other acyclic olefins such as *cis*-2-pentene, 1-pentene, and styrene, values as low as 1−2 turnovers per day have been reported.[6b,28c] Other chain-transfer agents are more effective.[7b]

Now that all of the rate constants are obtained, $\bar{X}_n$ can be calculated for any given reactant concentrations. Numerical calculations show that a larger concentration of neohexene has to be used to effect a measurable molecular weight change. Using these values, the experimental $\bar{X}_n$ values are in good agreement with the computational $\bar{X}_n$ values within the accuracies of the GPC instrument (Table 3).[35] Thus, the kinetics of the experimental system are adequately described by the simplified polymerization scheme in Figure 17.

## Conclusions

By expressing the kinetic equations governing the molecular weight distribution in terms of moments of distribution, the number-average degree of polymerization and polydispersity of a living system with added chain-transfer agents are computed. The temporal evolution of the concentrations of active and dead chains, monomer, catalyst, and chain-transfer agents is easily followed as well.

The computational results show that un-steady-state polymerizations exist in certain cases. The slope of the Mayo plot is not equal to the ratio $k_{tr}/k_p$ in general and varies from 0.5 to 1 order of magnitude when $k_{tr}/k_p = 0.01-1$. The variation is greater when $k_{tr}$ is much less than or much larger than $k_p$. The slope of the Mayo plot is also dependent on whether the experiment is conducted by varying the chain-transfer agent or the monomer.

Plots relating the slope of the Mayo plot to $k_{tr}/k_p$ for different values of $k_p/k_i$ have been constructed. There is but a narrow range of $k_{tr}/k_p$ where the addition of chain-transfer agent would allow a controlled variation of the molecular weight. This region corresponds to where $k_{tr}$ is equal to or an order of magnitude less than $k_p$. Huge $k_{tr}$ ($\gg k_p$) will not control the synthesis of low molecular weight polymers effectively, and a broad bimodal distribution results once all of the chain-transfer agent is consumed. A necessary but not sufficient condition to ensure monomodal distribution is that enough chain-transfer agents be present.

In the domain where $k_{tr} < k_p$, a steady-state approximation is applied (as warranted by numerical results) to derive an analytical solution for number-average degree of polymerization $\bar{X}_{ndead}$ (eq 23). The equation holds exactly when $[\text{catalyst}]_{initial} \ll [\text{chain-transfer agent}]_{initial}$. Similarly, an analytical expression relating the slope of the Mayo plot to $k_{tr}/k_p$ has also been obtained. The analytical results are in excellent agreement with the computational results.

Finally, by using ROMP of norbornene with molybdenum alkylidene in the presence of neohexene, the feasibility of using computation to predict the amount of chain-transfer agent needed to effect a visible change in molecular weight of the polymer is demonstrated. The experimental results show that the kinetics of this ROMP system can be adequately described by the polymerization scheme outlined in Figure 17.

For computation, only the two ratios $k_p/k_i$ and $k_{tr}/k_p$ are needed. The former can be obtained easily[16a] and the latter through the use of Mayo plot. Once these two parameters are known, the optimization of the relative amounts of reagents in a reaction to achieve particular molecular weight distributions can be realized computationally. The possibility of obtaining the same $\bar{X}_n$ and PDI using different ratios of the same reagents can be investigated as well.

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**Supplementary Material Available:** Plots of [chain]/[catalyst]$_{initial}$, % CTA consumed, $\bar{X}_n$, and PDI versus conversion of the monomer for various rate parameters, Mayo plots, and plots of Ss and $S_c$ versus $k_{tr}/k_p$ (16 pages). Ordering information is given on any current masthead page.

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(19) (a) Our notation $W_n$ corresponds to Pn* in some literature, while our $P_0$ corresponds to $T$. We note our notation $P_0$ is more appropriate because a chain-transfer agent can be viewed as a dead "polymer" chain with 0 units of monomer. (b) System where the reactivity of the initiating species produced by the reaction of the transfer agent with the active chain differs from that of the original initiating species will be treated in a future paper, as will other minor elaborations on the system (e.g., reactivation of a dead polymeric chain by an active chain). Claverie, J. P.; Benedicto, A. D.; Grubbs, R. H. Unpublished results.
(20) Figure 3 of ref 16a has been reproduced (see supplementary material).
(21) Moreover, if one were to isolate the polymers by addition of the reaction mixture into a nonsolvent, the oligomers might not precipitate out—which could lead one to isolate only the polymers with long chain lengths and narrow polydispersity and to falsely conclude that chain transfer rarely occurs.
(22) When the chain-transfer agent is consumed first, eventually all monomer is consumed, but the converse is not necessarily true.
(23) Mayo plot is a plot of $1/\bar{X}_n$ versus $[\text{chain-transfer agent}]_{\text{initial}}/[\text{monomer}]_{\text{initial}}$. The slope of the Mayo plot for a *non*living polymerization (whereby the chain-transfer agent is neither a monomer nor an initiator) is shown to be equal to the chain-transfer constant $C_s$—defined to be the ratio $k_{tr}/k_p$. To avoid confusion, in our plot (for living systems with deliberate addition of chain-transfer agent) we denote the slope by Ss. (see Ref 4) (b) The slope Ss is derived from a least-squares fit of $1/\bar{X}_{n\text{all}}$ with $[\text{chain-transfer agent}]_{\text{initial}}/[\text{monomer}]_{\text{initial}}$.
(24) Figure 10 presented here is a typical behavior observed from the wide range of values examined. In these cases, the reaction is followed to completion whereby all active chains have reacted with the chain-transfer agents; therefore, $\bar{X}_{n\text{all}} = \bar{X}_{n\text{dead}}$. In the interest of space, Mayo plots where [catalyst]/[monomer] ratio is kept constant while [transfer agent] is varied are not presented. However, the results are summarized in Figure 14.
(25) For example, when $k_i = k_p = k_{tr} = 1$ and catalyst:monomer:chain-transfer agent = 1:100:100, the concentration of active chains in the reaction varies from 4% to 50% of $[\text{catalyst}]_{\text{initial}}$ throughout the extent of reaction. Another example is when $k_i:k_p:k_{tr}$ = 1:10000:5, and catalyst:monomer:chain-transfer agent = 1:100:10.
(26) Equating eqs 2–4 to zero gives a difference equation of

$$W_n = \frac{1}{\left(1 + \frac{k_{tr} P_0}{k_p M}\right)^n} \frac{k_i}{k_p} W_0$$

resulting in the active chains having a Flory–Schulz molecular weight distribution. In the system considered in this paper, the active chains cannot be characterized by such a distribution.
(27) (a) It is interesting to compare the assumptions used in the third case of ref 17 and ours (e.g., CTA ≫ CAT). In particular, their $N_1^*$ is our $W_0$ if we set our $k_i = k_p$. (b) To avoid confusion, the slope of the Mayo plot derived from the analytical eq 24 will be denoted by $S_c$ as opposed to Ss.
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(31) (a) Diluting an NMR solution to the same concentration as that used in GC experiment would require a large quantity of deuterated solvent. (b) Each pulse sequence (including delay time) in the NMR takes about 5 s. Eight scans constitute a spectrum. Therefore, the free induction decay spectrum of the first scan would differ significantly from that of the eighth scan due to the rapid rate of the reaction, thus imparting a degree of uncertainty to the resultant NMR integrals. These difficulties are avoided when GC is used.
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