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Measurement of Initial Degree of Polymerization without Reactivation as a New Method To Estimate Rate Constants of Deactivation in ATRP

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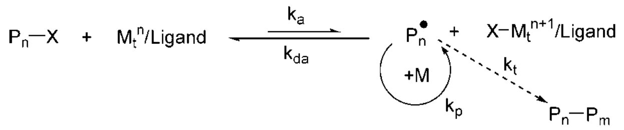
ABSTRACT: A new simple method has been developed for the estimation of deactivation rate constants in atom transfer radical polymerization using copper catalysts. This method is based on the principle of reverse ATRP and is conducted under an air atmosphere, using molecular oxygen as an oxidant for Cu(I) species. The deactivation rate constants for several different reactive copper complexes were estimated by this procedure, and the results are correlated with those obtained from the analysis of the evolution of molecular weight distribution with conversion and with competitive trapping reactions using nitroxides. The effect of temperature on these rate constants was also studied.

Introduction

Controlled/“living” radical polymerization (CRP) belongs to the most significant advances in polymer chemistry that have occurred during the past 10 years. Three primary CRP methods have been developed: atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition−fragmentation transfer polymerization (RAFT).[1,2] All three methods are very efficient synthetic tools providing well-defined polymers or copolymers with narrow molecular weight distributions ($M_w/M_n < 1.1$) and varied architectures (blocks, stars, brushes, combs).[3−11] The success of CRP lies in creating a dynamic equilibrium between a dormant species, present in large excess, and the active growing radical. In NMP and ATRP, this equilibrium occurs via activation/deactivation cycles, enabling the “living” behavior of the polymerization. In ATRP (cf. Scheme 1), the activation process corresponds to the generation of radicals $P_n^\bullet$, with the rate constant k_a, proceeding by a reversible homolytic cleavage of a carbon−halogen bond in a P_n−X species, catalyzed by a transition metal complex in a lower oxidation state n, M_t^n/ligand. These radicals can subsequently propagate with a rate constant k_p before deactivation takes place. In this step, radicals are deactivated with a rate constant k_{da}, by the higher oxidation state metal complex, X−M_t^{n+1}/ligand, to form the dormant species P_m−X; they may also participate in termination reactions with a rate constant k_t.

Scheme 1. General Scheme of ATRP



The correct selection of the components of an ATRP reaction allows creation of an appropriate equilibrium between activation and deactivation processes and enables a successful ATRP to occur. The equilibrium constant ($K_{eq} = k_a/k_{da}$) determines the concentration of radicals and, therefore, the rates of polymerization and termination. K_{eq} should be rather small, leading to a low instantaneous radical concentration and subsequently negligible termination. The effect of these constants and concentrations on kinetics and polydispersities are given more precisely in eqs 1 and 2.[4,12,13]

$$R_p = k_p \frac{k_a}{k_{da}}[I]_0 \frac{[M_t^{\,n}/L]}{[XM_t^{\,n+1}/L]}[M] \tag{1}$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[I]_0}{k_{da}[XM_t^{\,n+1}/L]}\right)\left(\frac{2}{p} - 1\right) \tag{2}$$

In these equations, $[I]_0$ refers to the initial concentration of the initiator (normally an alkyl halide). From eq 1, the rate of polymerization, R_p, is directly proportional to the equilibrium constant and the propagation rate constant. The rate increases with the concentration of activator, initiator and monomer, and decreases with deactivator concentration. Equation 2 shows that lower polydispersities are obtained with a low propagation rate constant, high conversion, and a fast deactivation rate constant, while higher initiator concentration and lower deactivator concentration lead to a broadening of the molecular weight distribution.

Consequently, given the significant influence of k_a and k_{da} on rate of polymerization and the polydispersity of the produced polymer, determination of these rate constants has been the subject of several studies.[14,15] In ATRP, two distinct approaches have been considered for the measurement of those rate constants. In one method, k_a was measured using macromolecular species along with GPC, ^{1}H NMR, and HPLC.[16−18] In the other approach, low molar mass models were studied. The procedure for the determination of k_a was based on kinetic isolation of the activation step from the deactivation process. The deactivation rate constant, k_{da}, was measured using either an inhibition periods in the presence of transition metal compounds[19] or a competitive kinetic experiment with formation of a TEMPO adduct as the clock reaction.[20,21] The latter procedure

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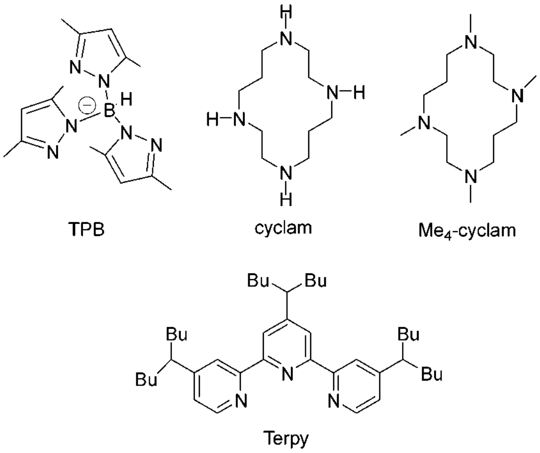
Chart 1. Ligands Used for k_{da} Estimation



can only be applied to model systems and becomes difficult for reactions exhibiting low deactivation rate constants when trapping of radicals by Cu(II) is much slower than radical combination with TEMPO. The deactivation rate constants were also estimated from the evolution of polydispersities as a function of conversion.[22,23]

We report here a new method for the estimation of deactivation rate constants of macromolecular species under genuine ATRP conditions with various Cu-based catalysts. This method, based on initial degrees of polymerization, is especially efficient when the rate constant of deactivation is relatively low. The advantages and limitations of the procedure are discussed and compared with the other methods.

Experimental Section

Materials. *n*-Butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%), and styrene (St, 99%; all from Aldrich) were vacuum-distilled over CaH_2 and stored under a nitrogen atmosphere at −15 °C. AIBN (Aldrich, 98%) was recrystallized from diethyl ether and stored at −15 °C. 1-Phenylethyl bromide (1-PEBr, Aldrich, 97%) was used as received without further purification. The ligands, potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride (TPB) (Acros, 98%), 1,4,8,11-tetraazacyclotetradecane (cyclam) (Aldrich, 98%), and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) (Aldrich, 98%), were used as received. Copper(II) bromide (Aldrich, 98%) and 1,4-dimethoxybenzene (Acros, 98%) were used without purification. 4,4,4-Tris(5-nonyl)-2,2:6,2-terpyridine (TERPY) was synthesized as reported earlier,[24] and the TPBCu(II)Br complex was prepared according to a literature procedure[25] (see Chart 1 for ligands structure).

Polymerization Procedure. Complexes of copper (I or II) with ligands, AIBN (when required), and 1,4-dimethoxybenzene were placed in a dry round-bottom Schlenk flask. The flask was sealed with a rubber septum and was degassed on a vacuum line (three vacuum/nitrogen cycles). Then degassed monomer was added using a previously purged syringe. The solution was stirred for 10 min at room temperature to fully dissolve the complex, leading to a homogeneous solution. The alkyl halide initiator was added, and the flask was immersed in an oil bath held by a thermostat at the desired temperature. At timed intervals, samples were withdrawn from the solution using a degassed syringe, dissolved in THF, and filtered through a column of alumina before analysis.

An example of a typical polymerization procedure: a dried 25 mL round-bottom Schlenk flask was charged with TPBCu(II)Br (19.2 mg, 4.36×10^{-5} mol), AIBN (4.2 mg, 2.6×10^{-5} mol), and 1,4-dimethoxybenzene (200 mg, 1.45×10^{-3} mol). The flask was sealed with a rubber septum and was degassed on vacuum line (three vacuum/nitrogen cycles). Then, the degassed monomer (styrene, 10 mL; 8.73×10^{-2} mol or *n*-butyl acrylate, 12.5 mL; 8.73×10^{-2} mol) was added using previously purged syringe. The solution was stirred for 10 min at room temperature to fully dissolve the complex, leading to a homogeneous solution. The alkyl halide initiator (1-phenylethyl bromide, 59 μL, 4.36×10^{-4} mol; or methyl 2-bromopropionate, 48 μL, 4.36×10^{-4} mol) was added, and the flask was immersed in an oil bath held by a thermostat at the desired temperature. At timed intervals, samples were withdrawn from the solution using a degassed syringe. After heating was stopped, the reaction mixture was cooled to room temperature, open to air, and diluted a fewfold with THF saturated with air. The solution was then passed over alumina to remove Cu complexes before analysis. In a typical styrene polymerization at 110 °C after 210 min of reaction, the results are the following: conversion, 75%; GPC, $M_n = 11\,250$; $M_w/M_n = 3.82$. In a *n*-butyl acrylate polymerization after 30 min at 90 °C, the results are the following: conversion, 93%; GPC, $M_n = 30\,100$; $M_w/M_n = 4.63$.

Deactivation Rate Constant Measurement. An example of a typical procedure: a dried 25 mL round-bottom flask was charged with TPBCu(II)Br (9.6 mg, 2.2×10^{-5} mol), AIBN (2.1 mg, 1.3×10^{-5} mol), and 1,4-dimethoxybenzene (200 mg, 1.45 $\times 10^{-3}$ mol). Styrene (10 mL, 8.73×10^{-5} mol) was added, and the solution was stirred at room temperature under an air atmosphere until complete homogenization of the reaction mixture (typically 15 min). Then, the flask was sealed with a rubber septum, again under an air atmosphere (headspace approximately 15 mL), and immersed in an oil bath held by a thermostat at the desired temperature. Samples were withdrawn from the solution without any inlet/outlet of gas, immediately cooled to room temperature in the presence of air, diluted a fewfold with THF saturated with air, and filtered through alumina to remove Cu complexes before analysis. In a typical deactivation rate constant experiment at 110 °C, after 6 min of reaction, the results are the following: conversion, 4%; GPC, $M_n = 8500$; $M_w/M_n = 1.70$.

Characterization. Monomer conversion was determined from the concentration of residual monomer by gas chromatography (GC) with 1,4-dimethoxybenzene as internal standard, using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Analysis conditions: injector temperature, 250 °C; detector temperature, 250 °C; temperature program, 2 min 70 °C, 40 °C/min until 180 °C, 2 min 180 °C. Molecular weights (relative to linear polystyrene standards) and molecular weight distributions were measured using a Waters 712 WISP autosampler equipped with 10^2, 10^3, and 10^5 Å PSS (Polymer Standards Services, Mainz, Germany) columns and a Waters 410 refractive index detector, using toluene as internal standard and THF as the eluent at 25 °C with a flow rate of 1 mL/min.

Results and Discussion

Among the various ATRP catalysts that have been evaluated, CuBr complexed with hydrotris(3,5-dimethyl-1-pyrazolyl)borate (TPB), 1,4,8,11-tetraazacyclotetradecane (cyclam), and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) exhibit very high activity. Unfortunately, polymerizations using these complexes were not well controlled, even using concurrent reverse and normal initiation,[26] which were recently developed for highly active systems. The results obtained for polymerization of *n*-butyl acrylate and styrene are shown in Table 1.

Molecular weights higher than predicted and broad molecular weight distributions were observed when using these active catalysts. A likely reason for poor control could be a low deactivation rate constant.

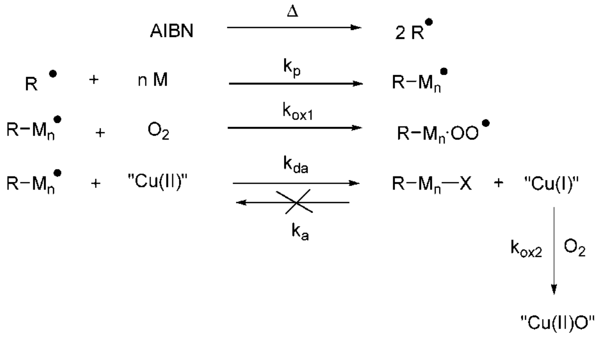
To verify this hypothesis, a new method for the determination of the deactivation rate constant in such systems was developed and applied to these polymeriza-

Table 1. "Reverse" ATRP of Styrene and BA Using TPB and Cyclam Derivatives as Ligands[a]

monomer	ligand	polymerization time (min)	conv (%)	M_n	M_w/M_n
St	TPB	210	75	11 250	3.82
BA	TPB	30	93	30 100	4.63
St	cyclam	15	53	38 200	1.85
BA	cyclam	10	67	59 500	4.95
St	Me_4-cyclam	420	30	18 700	1.93

[a] For styrene: $[St]_0 = 8.73$ M, $[1\text{-PEBr}]_0 = 0.0436$ M, $[AIBN]_0 = 0.0026$ M, $[Cu(II)/L]_0 = 0.0044$ M, 110 °C. For BA: $[BA]_0 = 6.97$ M, $[MBP]_0 = 0.035$ M, $[AIBN]_0 = 0.0021$ M, $[Cu(II)/L]_0 = 0.0035$ M, 90 °C.

Scheme 2. Ideal Pathway for Deactivation Rate Constant Measurement



tions. This method is based on the principle of reverse ATRP under homogeneous conditions,[27] which has been successfully extended to polymerizations using highly active catalyst systems by combining simultaneously reverse and normal initiation processes.[26] The prerequisite for this approach of measurement of deactivation rate constants is that the generated Cu(I) complexes should react quickly with O_2 to form inactive μ-oxo or/and μ-peroxo Cu(II) complexes.[28,29] These reactions are well documented because of the use of oxo–copper complexes as an oxygen transport protein.[30] Scheme 2 presents relevant elementary reactions involved in reverse ATRP under aerobic conditions.

Radicals formed by thermal decomposition of AIBN react with monomer (M) to yield polymeric radicals, until either deactivated by an atom transfer reaction with the Cu(II) complex to give a polymer with a terminal halogen and a Cu(I) species or trapped by oxygen. Oxygen reacts preferentially with Cu(I) species, which are present at much higher concentrations than the active radicals, to form oxo, peroxo, or other more stable Cu(II) complexes, which cannot (re)activate the halogenated polymeric chains (kox_2). In a separate experiment, the fully oxidized Cu(II) species did not activate ATRP process. The use of oxygen as a scavenger has already been described for the determination of the rate coefficient for C–O bond homolysis in alkoxyamines.[31]

Under these conditions, at low degrees of conversion, the deactivation rate constant, which is the only unknown parameter in eq 3, should be easy to determine.

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + \frac{k_{da}[Cu(II)]_0}{k_p[M]_0} \qquad (3)$$

Accordingly, a series of polymerizations using different complex concentrations, ligands, and monomers were performed under aerobic conditions at different temperatures.

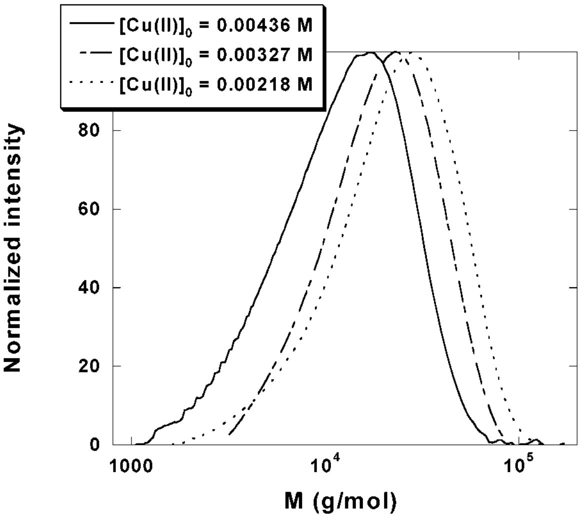


Figure 1. Molecular weight distributions obtained for the bulk polymerization of styrene with TPB as ligand under aerobic conditions. $[St]_0 = 8.73$ M, $[AIBN]_0 = 0.0013–0.0026$ M, $[Cu(II)/L]_0 = 0.0022–0.0044$ M, 6 min at 110 °C.

Results with TPB/CuBr$_2$. A series of experiments were conducted at different initial Cu(II) concentrations and samples for GPC analysis were taken 6 min after initiation of the polymerization. Similar monomodal GPC traces were obtained with polydispersities $M_w/M_n \approx 1.70$. When a concentration of $[Cu(II)]_0 = 4.36 \times 10^{-3}$ M was used, the monomer conversion was only 4%, the number-average molecular weight, measured by GPC, was $M_n = 8.46 \times 10^3$ g/mol, corresponding to a degree of polymerization of 81, which agrees well with the molecular weight obtained and the number of chains expected on the basis of the calculated number of chains generated by AIBN decomposition. Similar agreement was observed for different initial Cu(II) concentrations.

The GPC chromatograms for the polymers prepared in this series of experiments with a range of $[Cu(II)]_0$ concentrations are shown in Figure 1. Although the polydispersities are rather high ($M_w/M_n \approx 1.70$), a clear separation of the different traces is observed. The reactions were stopped by cooling to room temperature after short reaction time (6 min) to avoid any significant changes in conversion of monomer and [Cu(II)] species to simplify the use of eq 3. According to this equation, at a given temperature, the reciprocal value of the degree of polymerization should be a linear function of $[Cu(II)]_0$. As shown in Figure 2, when the initial copper(II) concentration was varied from 0.0022 to 0.0044 M, $1/DP_n$ increased linearly with increasing concentration of $[Cu(II)]_0$. Since the slope is equal to ($k_{da}/k_p[M]_0$), an average value for k_{da} can be easily estimated. In this case, with $k_p = 1.6 \times 10^3$ M^{-1} s^{-1},[32] the average value is $k_{da} = (4.3 \pm 1.0) \times 10^4$ M^{-1} s^{-1}. This value is too low for a successful ATRP to be conducted and could explain the uncontrolled polymerizations. Typical values for k_{da} with efficient ATRP catalysts are in the range $10^6–10^7$ M^{-1} s^{-1}.[16,20,21]

The effect of temperature on k_{da}, for systems employing TPB/CuBr$_2$ as catalyst and styrene as monomer, was also investigated. The lowest temperature employed should be high enough to enable AIBN thermal decomposition and provide a sufficient rate of propagation. The range of temperature examined was 90–135 °C. Figure 3 shows the Arrhenius plot. The activation energy is equal to $E_a = 52 \pm 4$ kJ/mol, and the preexponential

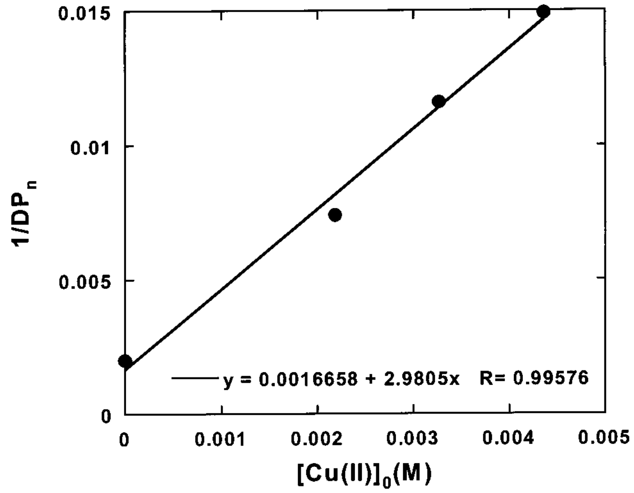


Figure 2. Reciprocal value of the degree of polymerization as a function of $[Cu(II)]_0$ for the bulk polymerization of styrene with TPB as ligand. $[St]_0 = 8.73$ M, $[AIBN]_0 = 0.0013-0.0026$ M, $[Cu(II)/L]_0 = 0.0022-0.0044$ M, 6 min at 110 °C.

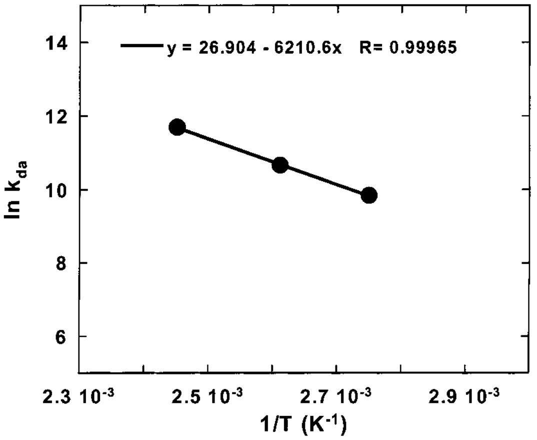


Figure 3. Effect of the temperature on k_{da} for the bulk polymerization of styrene with TPB as ligand. $[St]_0 = 8.73$ M, $[AIBN]_0 = 0.0026$ M, $[Cu(II)/L]_0 = 0.0022$ M, 90–135 °C.

factor is equal to 4.8×10^{11} s^{-1}. Enthalpy and entropy factors at 298 K can be estimated from these constants. The enthalpic term is rather high for a reaction between radicals, $\Delta H^{\ddagger} = 49$ kJ/mol, and the entropy of activation, $\Delta S^{\ddagger} = -80$ J/(K mol), is much less negative than expected for a bimolecular reaction, perhaps due to some additional rotational and vibrational entropy penalty during the Cu(II)–Cu(I) transition.

Effect of Monomer Structure. This method for measurement of the deactivation rate constant is quite general and can also be applied to other monomers such as *n*-butyl acrylate and methyl methacrylate. Measurements were conducted at 90 °C for both monomers with TPB/$CuBr_2$ as catalyst. Using values of $k_p(BA) = 56.4 \times 10^3$ M^{-1} s^{-1} and $k_p(MMA) = 1.58 \times 10^3$ M^{-1} s^{-1},[32] deactivation rate constants equal to 3.5×10^5 and 1.4×10^4 M^{-1} s^{-1} were obtained for BA and MMA, respectively. These results are different than those obtained for styrene (Table 2). For BA, k_{da} is about 10 times larger than the value obtained for styrene, while for MMA it is slightly lower.

Table 2. Values of k_{da} Measured under an Air Atmosphere with TBP as Ligand: Effect of Monomer Structure[a]

monomer	temp (°C)	k_{da} (M^{-1} s^{-1})	k_{da}/k_p	$k_{da}/k_{(St)}$
St	110	4.3×10^4	26	26
St	90	3.0×10^4	20	20
MMA	90	1.4×10^4	8.8	4.4
BA	90	3.5×10^5	6.2	1.2

[a] Bulk polymerizations; $[Cu(II)]_0 = 0.0022$ M; $[AIBN]_0 = 0.0013$ M, reaction time, 6–25 min.

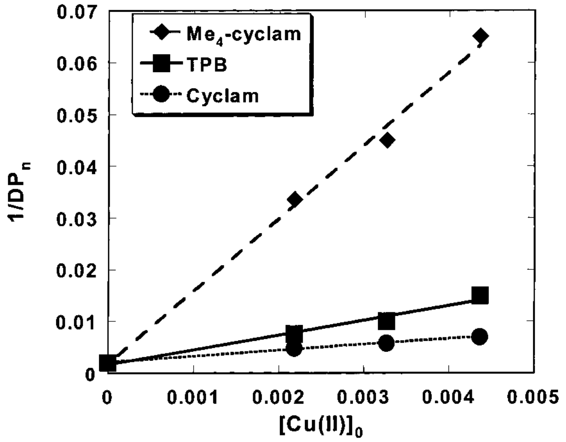


Figure 4. Reciprocal value of the degree of polymerization as a function of $[Cu(II)]_0$ for the bulk polymerization of styrene with TPB, cyclam, and Me_4-cyclam as ligand. $[St]_0 = 8.73$ M, $[AIBN]_0 = 0.0013-0.0026$ M, $[Cu(II)/L]_0 = 0.0022-0.0044$ M, 6 min at 110 °C.

The deactivation rate constant can be compared with the propagation rate constant for the growing radicals to the same standard monomer, i.e., styrene. These values were determined from the reactivity ratios $r_{MMA/S} = 0.50$[33] and $r_{BA/St} = 0.22$,[34] i.e., $k_{da}/k_{(St)} = (k_{da}/k_p)r$. A polystyryl radical reacts with the TPB/Cu(II) complex 30 times faster than with styrene. This ratio decreases to ~5 for a pMMA radical and to ~1 for the poly(butyl acrylate) radical.

The differences in the absolute rate constants have obvious origins in the overall reactivity and stability of the radical. The ratios indicate some radical selectivities. The more nucleophilic styryl radical has apparently the highest affinity for bromine abstraction, whereas the most electrophilic pBA radical has the lowest. This agrees well with general trends observed in atom transfer reactions.[19,35–37] Additionally, some steric effects and reaction medium effects cannot be completely discarded.

Effect of Ligand. The 1,4,8,11-tetraazacyclotetradecane/$CuBr_2$ complex was used for a study similar to that conducted with TPB. Variation of the initial copper(II) concentration enables observation of the linear dependence of $1/DP_n$ vs $[Cu(II)]_0$, as shown in Figure 4. In this case, k_{da} calculated from the slope of $1/DP_n = f([Cu(II)]_0)$ is $k_{da} = 1.8 \times 10^4$ M^{-1} s^{-1}, i.e., a value even lower than the one obtained for k_{da} (TPB). This result is consistent with the faster reverse ATRP of styrene noticed with cyclam as ligand (Table 1). This result may be additionally magnified by a higher k_a, which scales reciprocally with a low k_{da}. The same study performed with the permethylated cyclam (Me_4-cyclam) ligand shows the effect of substitution of the amine on k_{da}. Indeed, from the usual $1/DP_n = f([Cu(II)]_0)$ plot, $k_{da} = 1.6 \times 10^5$ M^{-1} s^{-1} was estimated, yielding a value 10 times higher than the one observed for cyclam. This trend is consistent with the polymerization data and has also been noticed for tris(2-aminoethyl)amine (TREN) derivatives. Me_6-TREN associated with CuBr forms the most active catalyst in ATRP,[38,39] but the use of the

Table 3. Values of k_{da} Calculated for TBP Using Eq 2

monomer (conv)[a]	M_n (g/mol)	M_w/M_n	$k_{da(PDI)}$[b] ($M^{-1}\ s^{-1}$)	$k_{da(DP)}$[c] ($M^{-1}\ s^{-1}$)
A: St (36%)	4200	2.70	4.3×10^4	4.3×10^4
B: St (69%)	2300	1.60	1.2×10^4	4.3×10^4
C: BA (93%)	30100	4.63	2.0×10^5	3.5×10^5

[a] A: $[St]_0 = 8.73$ M, $[1\text{-PEBr}]_0 = 0.0436$ M, $[AIBN]_0 = 0.0026$ M, $[Cu(II)/L]_0 = 0.0044$ M, 110 °C. B: $[St]_0 = 8.73$ M, $[1\text{-PEBr}]_0 = 0.1000$ M, $[AIBN]_0 = 0.0100$ M, $[Cu(II)/L]_0 = 0.0400$ M, 110 °C. C: $[BA]_0 = 6.97$ M, $[MBP]_0 = 0.035$ M, $[AIBN]_0 = 0.0021$ M, $[Cu(II)/L]_0 = 0.0035$ M, 90 °C. [b] Calculated using eq 2. [c] Estimated using oxygen trapping.

nonmethylated TREN leads to an uncontrolled polymerization, which may be due to a lower value for k_{da}. Extrapolation to $[Cu(II)]_0 = 0$ with three different ligands yields average value DP = 520 (Figure 4). When the polymerization was carried out without any Cu(II) species, the initial degree of polymerization was DP = 509. This demonstrates the validity of the method based on the measurement of initial degree of polymerization without reactivation.

Validity of the New Approach. The values of k_{da} obtained using this new method were directly compared with the values determined by either the evolution of PDI with conversion according to eq 2 or by competitive trapping using nitroxides.

Equation 2 was originally developed for the exchange reactions between polystyryl free anions and ion pairs[40] and was later applied to the living carbocationic systems[41] and to the controlled/living radical polymerization.[12,23,42] Kinetics of exchange reactions in many polymerizations with intermittent activation can be studied by using evolution of PDI with conversion.[13] When PDI are analyzed as a function of time, a similar equation can be used which provides access to the rate constant of activation and does not require knowledge of the deactivator concentration.[15] In general, such treatment requires complete initiation and minimal contribution of chain breaking reactions.[43]

Equation 2 was applied to estimate k_{da} for styrene polymerization at 110 °C, using simultaneous reverse and normal initiation processes with TPBCu(II). The calculations were made for a long reaction time to allow a complete AIBN decomposition and therefore the establishment of the ATRP equilibrium. In addition, [Cu(II)] equal to ~10% $[Cu(II)]_0$ was used for the calculations, based on results obtained by EPR.[44] The calculated results ($k_{da(PDI)}$) from one point experiment agrees well with the values obtained using measurement of initial degree of polymerization ($k_{da(DP)}$) (Table 3). The average value estimated from the initial DP for styrene is $k_{da(DP)} = 4.3 \times 10^4\ M^{-1}\ s^{-1}$, while the average value calculated from the evolution of polydispersities is $k_{da(PDI)} = 2.7 \times 10^4\ M^{-1}\ s^{-1}$. For BA polymerization, a value approximately 10 times higher was obtained from initial DP method ($k_{da(DP)} = 3.5 \times 10^5\ M^{-1}\ s^{-1}$), which also correlates with much higher value obtained for evolution of PDI ($k_{da(PDI)} = 2.0 \times 10^5\ M^{-1}\ s^{-1}$).

This comparison was also carried out for TERPY, cyclam, and Me_4-cyclam as ligands for styrene polymerization. The evolution of polydispersity with conversion for TERPY is reported in Figure 5. The polydispersity decreases with conversion, and the estimated average k_{da} values ($k_{da(PDI)} = 6 \times 10^5\ M^{-1}\ s^{-1}$) are similar to those obtained by measurement of the initial degree of polymerization ($k_{da(DP)} = 1 \times 10^6\ M^{-1}\ s^{-1}$) (Table 4). For both cyclam and Me_4-cyclam, the deactivation rate constants, calculated from eq 2, are not consistent with the values estimated with the measurement of the initial degree of polymerization. The use of cyclam and Me_4-cyclam may illustrate the limitation of eq 2 for the determination of deactivation rate constants. Equation 2 can only be applied under ATRP conditions, when initiation is completed and the proportion of dead chains is low.[43,45] Moreover, it requires a precise knowledge of the concentration of the deactivator, and the discrepancies may be due to the underestimated [Cu(II)], which should be measured directly by for example EPR.

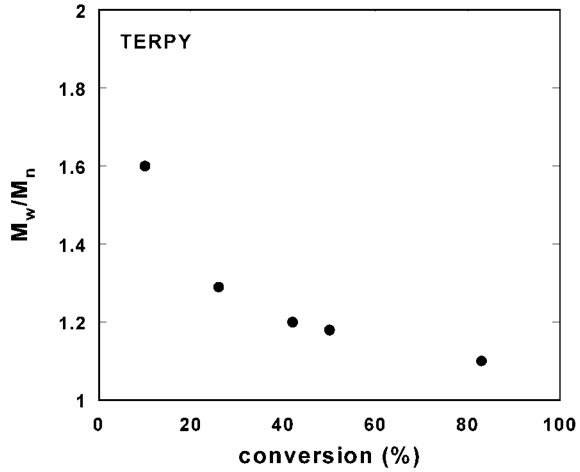


Figure 5. Evolution of polydispersity with conversion for styrene polymerization with TERPY as ligand. $[St]_0 = 8.73$ M, $[1\text{-PEBr}]_0 = 0.088$ M, $[Cu(I)/L]_0 = 0.088$ M, 110 °C.

Table 4. Values of $k_{da(DP)}$ and $k_{da(PDI)}$: Effect of Ligand Structure[a]

monomer	ligand	temp (°C)	$k_{da(DP)}$ ($M^{-1}\ s^{-1}$)	$k_{da(PDI)}$ ($M^{-1}\ s^{-1}$)
St	TPB	110	4.3×10^4	2.7×10^4
St	TPB	90	1.8×10^4	
BA	TBP	90	3.5×10^5	2.0×10^5
St	cyclam	110	1.8×10^4	
St	Me_4-cyclam	110	2.0×10^5	
St	TERPY	110	1.0×10^6	6.0×10^5
BA	TERPY	75	9×10^5	
1-PEBr[b]	TERPY	75	4.1×10^5	

[a] Bulk polymerizations; $[Cu(II)]_0 = 0.0044$ M; $[AIBN]_0 = 0.0026$ M, reaction time, 6–15 min. [b] Measurement performed in acetonitrile using model compounds.[20]

This new method for determining deactivation rate constants has also been compared with model studies using 1-(*N*,*N*-(2-methylpropyl-1)(1-diethylphosphono-2,2-dimethylpropyl-1)-*N*-oxyl)-1-phenylethane (PESG1) as the generator of a styryl radical for a "TERPY/$CuBr_2$" catalytic system.[20] ATRP with TERPY complex is a better-controlled system than with TBP or cyclam ligands.[24] To obtain a sufficient degree of polymerization from styrene polymerization for GPC measurement, the reaction was carried out at 110 °C. A deactivation rate constant of $k_{da} = 1.0 \times 10^6\ M^{-1}\ s^{-1}$ was obtained. This value could be extrapolated to lower temperatures, giving a value of $k_{da} = 4.3 \times 10^5\ M^{-1}\ s^{-1}$ at 75 °C, assuming a similar activation energy as for TPB Cu(II)Br complex. The latter value is close to that measured for a model 1-phenylethyl radical at 75 °C in acetonitrile ($k_{da} = 4.1 \times 10^5\ M^{-1}\ s^{-1}$).[20] The agreement between the measured values may indicate that the new method for the determination of the rate constant of deactivation is valid since it generates values for the rate constants that are consistent with earlier measurements. It also suggests that differences between model systems and macromolecular systems are not very significant, at least for the TERPY/$CuBr_2$ complex, although lower values of deactivation rate constants could be expected for macromolecular systems due to steric constrains. A value of the same magnitude was also obtained using aerobic polymerization of BA. In bulk, using $[TERPY/Cu(II)Br_2]_0 = 0.0022$ M and $[AIBN]_0 = 0.0026$ M, $DP_n = 159$ was obtained at low conversion. Therefore, $k_{da} = 9 \times 10^5$ M^{-1} s^{-1} was calculated from eq 2 using $k_p = 4.6 \times 10^4$ M^{-1} s^{-1}.[46]

General Requirements for k_{da} Determination. The parameters in eq 3 are readily accessible. DP_n can be obtained by GPC ($DP_n = M_n/M_0$), k_p is available from pulse laser polymerization measurements reported in the literature,[46] and $[M]_0$ and $[Cu(II)]_0$ are variables depending on reaction conditions. However, this approach can only be applied when the following conditions are satisfied:

1. The reliable range k_{da}/k_p is limited by the GPC range and values of DP_{n0} ($10 \leq DP \leq 10^3$), the amount of polymer available for analysis (≥0.1 wt %), the range of $[Cu(II)]_0$ due to the solubility and sensitivity to impurities (10^{-3} M $\leq [Cu(II)]_0 \leq 10^{-1}$ M), and the monomer concentration (1 M $\leq [M]_0 \leq$ 10 M). One can calculate the highest accessible value of $k_{da}/k_p = 10^3$, using $[Cu(II)]_0/[M]_0 \approx 10^{-4}$ and targeting DP = 10, and the lowest $k_{da}/k_p = 10^{-1}$, by using $[Cu(II)]_0/[M]_0 \approx 3 \times 10^{-2}$ and DP = 300. Nevertheless, the accessible range of k_{da}/k_p ratios is quite large ($10^{-1} \leq k_{da}/k_p \leq 10^3$). For example, the range of determinable k_{da} for both styrene at 110 °C and MMA at 90 °C is 2×10^2 M^{-1} $s^{-1} \leq k_{da} \leq 2 \times 10^6$ M^{-1} s^{-1} while it is 4×10^4 M^{-1} $s^{-1} \leq k_{da} \leq 6 \times 10^7$ M^{-1} s^{-1} for BA at 90 °C.

2. To prevent reaction of the deactivated species with Cu(I), the oxidation rate of the Cu(I) species (R_{ox2}) should be high compared to the rate of activation (R_{act}) (eq 4). Typical values of the oxidation rate constant k_{ox2} are between 10^6 and 10^8 M^{-1} s^{-1},[47] while values observed for k_a are between 0.02 and 2 M^{-1} s^{-1}.[20,21] Furthermore, the initial oxygen concentration found in the usual organic solvents is around 2×10^{-3} M under 0.21 atm of O_2, i.e., under air atmosphere.[48] When all of these parameters are taken into account, the validity of eq 4 seems to be verified.

$$k_{ox2}[O_2]_0[Cu(I)]_0 > k_a[RX]_0[Cu(I)]_0 \qquad (4)$$

3. To obtain polymers of sufficient DP, the oxidation rate of radicals by O_2 (R_{ox1}) should be lower than to the rate of propagation (R_p) (eq 5). Using values range between 4×10^6 and 5×10^9 M^{-1} s^{-1} for k_{ox1} (the lowest values were found for stabilized radicals such as the styryl radical)[49,50] and calculated k_p values,[32] condition (5) is met.

$$k_p[M]_0[R^\bullet] > k_{ox1}[O_2]_0[R^\bullet] \qquad (5)$$

4. Termination should be slower than propagation (eq 6). For eq 6, a value of $k_t = 3 \times 10^8$ M^{-1} s^{-1} was used.[51] Again the conditions are valid.

$$k_p[M]_0[R^\bullet] > k_t[R^\bullet]^2 \qquad (6)$$

5. The radicals should not react with the copper complexes to form organometallic species. Some interaction of propagating radicals with copper complexes has been reported, but the results show that under the conditions used in this study such interaction is insignificant.[52]

Nevertheless, when the oxygen concentration is too low, the reactivation can occur, and molecular weights no longer describe initial conditions. On the other hand, when $[O_2]$ is too high, it can also react with growing radicals and limit the degree of polymerization. Therefore, a precise control of $[O_2]$ is recommended, and further work in this area is needed. Moreover, reactions should be stopped at the lowest possible conversion to prevent significant changes not only in monomer but also in deactivator structure and concentration.

Conclusion

We have described a new method for the estimation of the deactivation rate constant under real ATRP conditions. This technique is based on a reverse ATRP process in the presence of O_2. The results agree relatively well with values obtained using different techniques. The method is applicable to a large range of monomers (styrene, acrylates, and methacrylates), at different temperatures (from 70 to 135 °C), allowing a wide range of k_{da} values to be estimated and is especially well-suited to reactions with relatively slow deactivation. However, some prerequisites on the range of conversion, k_{da}/k_p, and monomer, oxygen, and Cu(II) concentrations are needed for this method to provide reliable estimates of the deactivation rate constants.

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