Effect of the Copper Counterion on the Activation Rate Parameter in Atom Transfer Radical Polymerization

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ABSTRACT: The activation rate parameter (k_{act}) in atom transfer radical polymerization (ATRP) for a poly(ethylene-*co*-butylene) (PEB) macroinitiator bearing a bromoisobutyryl initiating group catalyzed by CuBr/2L and CuCl/2L (L = *N*-*n*-pentyl-2-pyridylmethanimine) has been determined using the nitroxide exchange reaction with hydroxy-TEMPO in combination with gradient polymer elution chromatography (GPEC). With GPEC and ^{1}H NMR analyses, the fraction of activated chains that is terminated via combination with hydroxy-TEMPO was estimated at 95%. Concentrations of the activating copper(I) complexes during the exchange experiments have been determined using UV−vis spectroscopic measurements. Compared to bromide, the use of chloride as the copper counterion results in a strong increase in k_{act} by more than a factor of 2. The improved control in ATRP for mixed halide initiating systems as R−Br/CuCl compared to R−Br/CuBr systems is therefore not entirely attributed to an increased ratio of initiation to propagation rate through halogen exchange, but also finds its origin in an increased rate of activation.

Introduction

One of the most applied polymerization techniques in the field of living radical polymerization is atom transfer radical polymerization (ATRP).[1,2] ATRP allows the preparation of a vast range of polymeric materials with controlled molecular weights and well-defined chain architectures.[3] The control of polymerization in ATRP relies on the reversible activation of a dormant alkyl halide species through halogen abstraction by a transition metal complex, which is mostly copper based. To ensure a good control over the molecular weight and molecular weight distribution,[4] a low equilibrium constant (k_{act}/k_{deact}) is required in order to maintain a low radical concentration, thereby reducing the probability of termination reactions. Narrow molecular weight distributions are obtained when the deactivation of the growing species is fast compared to propagation. Furthermore, the activation of the alkyl halide initiator should be as fast as or, more preferably, faster than the consecutive activation steps of dormant species, implying a simultaneous growth of polymeric species.

Although the ATRP process is considered to proceed according to the free-radical polymerization mechanism,[5] the mechanistic and kinetic features of ATRP regarding the role of the activating catalyst complex are hardly elucidated. Recently, we studied the effect of the copper counterion on the conversion rate of a bromine-functional polyolefin macroinitiator during the ATRP of methyl methacrylate (MMA), using gradient polymer elution chromatography (GPEC) in combination with evaporative light scattering detection (ELSD).[6] It was found that application of copper(I) chloride (CuCl) resulted in a much faster macroinitiator conversion than when copper(I) bromide (CuBr) was used, where both catalysts were ligated by *N*-*n*-pentyl-2-pyridylmethanimine (PPI). The use of a mixed halide initiating system as R−Br/CuCl is known to give an increased control of the molecular weight distribution, which is attributed to the preferential end-capping of the activated polymer chains by chloride over bromide.[7−9] The activation of the alkyl halide initiator involves breaking the weaker carbon−bromine bond, whereas after deactivation of the growing polymer chain through chloride end-capping, the activation of the dormant species requires breaking the stronger carbon−chlorine bond. In other words, the relative rate of initiation to that of propagation is increased, where initiation represents the first complete activation−monomer addition−deactivation cycle where the alkyl halide initiator is converted into the dormant species. Furthermore, Matyjaszewski and co-workers[7] reported that an equilibrium concentration of 80-90% R−Cl was reached within short time for several mixed halide systems with CuCl and CuBr catalysts ligated by 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy). Their measurements were based upon gas chromatographic and ^{1}H NMR spectroscopic analyses. Haddleton et al.[9] investigated halogen exchange during the ATRP of MMA in xylene catalyzed by PPI ligated CuBr and CuCl, using *p*-toluenesulfonyl bromide and chloride as initiators. Their results obtained from ^{13}C NMR studies differ from those reported by Matyjaszewski et al.[7] in that chloride end-capped PMMA is obtained exclusively, which implies different exchange mechanisms. Besides the limited understanding of the role of the catalyst complex on the halogen exchange dynamics, there is also little knowledge on the effect of the copper counterion on the activation rate parameter (k_{act}). Goto and Fukuda[10] have determined k_{act} for 1-phenylethyl bromide (PEBr) with diheptyl-2,2′-bipyridine (dHbpy) ligated CuBr and CuCl using the nitroxide trapping method together with ^{1}H NMR. They found a somewhat higher value of k_{act} for the PEBr/CuCl than for the PEBr/CuBr system (respectively 0.52 and 0.42 L mol^{-1} s^{-1}). Furthermore, k_{act} for 1-phenylethyl chloride was almost twice as high for CuCl/dHbpy than for CuBr/dHbpy (respectively 0.018 and 0.010 L mol^{-1} s^{-1}). The results obtained by Goto and Fukuda[10] indicate that the use of CuCl leads not only to an increased ratio of initiation to propagation rate through halogen exchange but also to a faster activation of the initiating species.

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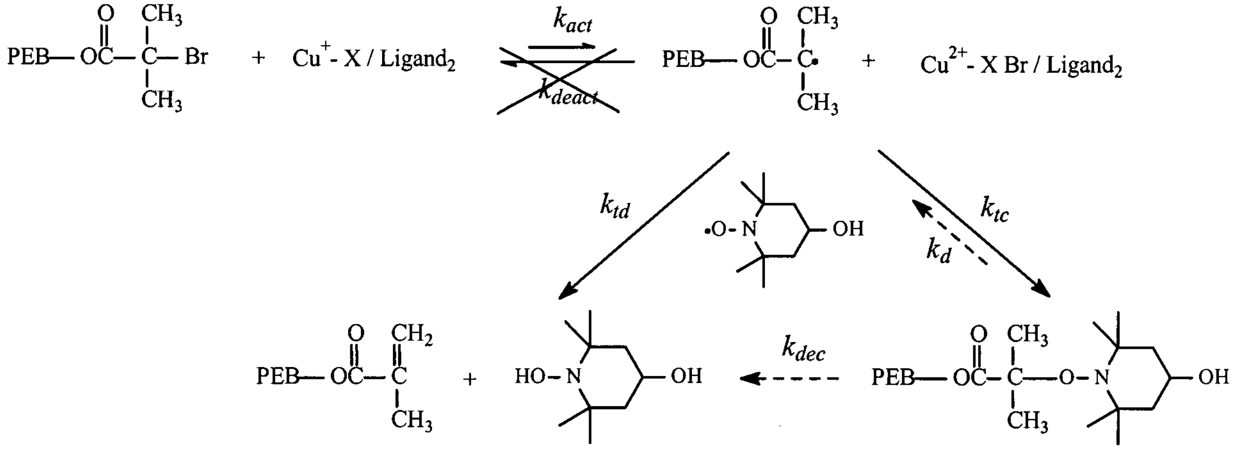
Scheme 1. Exchange Experiments of a Bromine-Functional Poly(ethylene-*co*-butylene) (PEB) Macroinitiator in the Presence of a Large Excess of Hydroxy-TEMPO; Activated Species Are Terminated via Combination (k_{tc}) or Disproportionation (k_{td}) with Hydroxy-TEMPO



To the best of our knowledge, activation rate parameters in ATRP for methacrylate dormant species have never been reported. The work in this paper describes the determination of k_{act} for a poly(ethylene-*co*-butylene) (PEB) macroinitiator bearing a bromoisobutyryl (MMA-like) initiating group with *N*-*n*-pentyl-2-pyridylmethanimine (PPI) ligated CuBr and CuCl. Experimental evidence is provided that the type of copper counterion significantly affects the activation rate constant.

Method

The applied method for the determination of the activation rate parameter is a combination of nitroxide-exchange experiments with quantitative HPLC, as recently reported by Chambard et al.[11] They used this method for investigating the effect of solvent in ATRP on k_{act} for polystyrene and poly(butyl acrylate) macroinitiators. As shown in Scheme 1, the exchange experiments are based on activation of the PEB−Br macroinitiator and subsequent irreversible trapping by a stable free radical, hydroxy-TEMPO. By utilizing a large excess of hydroxy-TEMPO, the probability that the radicals originating from the macroinitiator are deactivated rather than terminated is negligible.[11] The decrease in PEB−Br concentration ([P−Br]) is described by eq 1. Equation 2 presents the general solution when taking into account that also the copper(I) concentration decreases in time.

$$-\frac{\mathrm{d}[\mathrm{P-Br}]}{\mathrm{d}t} = k_{\mathrm{act}}[\mathrm{P-Br}][\mathrm{Cu(I)}] \qquad (1)$$

$$\ln\left(\frac{[\mathrm{P-Br}]_0}{[\mathrm{P-Br}]_t}\right) + \ln\left(\frac{[\mathrm{Cu(I)}]_0 - [\mathrm{P-Br}]_0 + [\mathrm{P-Br}]_t}{[\mathrm{Cu(I)}]_0}\right) = ([\mathrm{Cu(I)}]_0 - [\mathrm{P-Br}]_0)k_{\mathrm{act}}t \qquad (2)$$

where eq 2 can be abbreviated as eq 3:

$$\ln A + \ln B = Ck_{\mathrm{act}}t \qquad (3)$$

The hydroxy-functional species (PEB−OH) are separated from the macroinitiator chains using gradient polymer elution chromatography (GPEC). The decrease in P−Br concentration is obtained by means of evaporative light scattering detection (ELSD). Conventional nitroxides, such as TEMPO and derivatives thereof, are however known to cause hydrogen abstraction at elevated temperatures.[12,13] Especially for methacrylate-like tertiary carbon-centered radicals, a substantial fraction is terminated via disproportionation (k_{td}),[14,15] as depicted in Scheme 1. The separation of this termination product from the residual macroinitiator with GPEC is however much more difficult compared to the separation of the trapped hydroxy-functional species, which clearly hampers the determination of k_{act}. With the disproportionation product eluting at the same time as the residual macroinitiator, and assuming a constant ratio of termination via disproportionation (k_{td}) and termination via combination with the nitroxide (k_{tc}), the exact macroinitiator concentration $[\mathrm{P-Br}]_t$ can be calculated from the concentration as determined with GPEC, $[\mathrm{P-Br}]_{t,\mathrm{GPEC}}$, using eq 4:

$$[\mathrm{P-Br}]_t = \frac{1}{f_{\mathrm{tc}}}[\mathrm{P-Br}]_{t,\mathrm{GPEC}} - \frac{1-f_{\mathrm{tc}}}{f_{\mathrm{tc}}}[\mathrm{P-Br}]_{0,\mathrm{GPEC}} \qquad (4)$$

where f_{tc} ($0 < f_{\mathrm{tc}} < 1$) is the fraction of activated chains that is terminated by combination with hydroxy-TEMPO. Furthermore, the exact concentrations of Cu(I)Cl and Cu(I)Br during the exchange experiments are determined via UV−vis spectroscopic measurements as these catalysts have different solubility properties.

Experimental Section

Materials. *p*-Xylene (Aldrich, 99+% HPLC grade), CuBr (Aldrich, 98% and 99.999%), CuCl (Aldrich, 99+% and 99.995+%), and 4-hydroxy-TEMPO (Aldrich) were used without further purification. Catalysts of high purity were stored and weighed in a glovebox. The ligand *N*-*n*-pentyl-2-pyridylmethanimine (PPI) was synthesized as described by Haddleton et al.[16] and distilled prior to use. The bromine-functional poly(ethylene-*co*-butylene) macroinitiator (PEB−Br) was synthesized through esterification of hydroxy-functional poly(ethylene-*co*-butylene) (Kraton L-1203 (Shell Chemicals), M_n = 3700 g/mol, hydroxyl functionality >0.9, M_w/M_n = 1.07) with 2-bromoisobutyryl bromide; experimental details are given elsewhere.[6]

Exchange Experiments with Hydroxy-TEMPO. All exchange reactions were carried out in a 150 mL three-necked flask, equipped with magnetic stirrer. A polystyrene standard with a narrow molar mass distribution is added to the exchange reaction mixtures for normalization of the GPEC chromatograms. The PEB−Br macroinitiator (0.40 g, 1.03×10^{-4} mol), the polystyrene standard ($M_n = 68 \times 10^3$ g/mol, M_w/M_n = 1.07:0.16 g, 2.35×10^{-6} mol), hydroxy-TEMPO (0.35 g, 2.0×10^{-3} mol), and ligand (PPI: 0.16 g, 9.1×10^{-4} mol) were dissolved in 18 g of *p*-xylene. The mixture was homogenized and purged with argon for about 30 min. The copper catalyst (Cu(I)Br: 0.047 g, 3.28×10^{-4} mol or Cu(I)Cl: 0.032 g, 3.28×10^{-4} mol) was subsequently added under argon flow, and the mixture was purged with argon for another 15 min. A sample was taken from the reaction mixture as reference for the GPEC analysis (t_0 sample), after which the flask was immersed in a thermostatically controlled oil bath at 90 °C. Samples were taken at timed intervals through a septum and quenched in liquid nitrogen. Prior to the GPEC analyses, the reaction samples were purified from copper by passing them over an activated alumina column.

UV−Vis Measurements. The spectroscopic UV−vis measurements were performed at 20 °C on a Hewlett-Packard UV−vis spectrometer, using a quartz UV cell. Stock solutions of Cu(I)Br/PPI and Cu(I)Cl/PPI in deoxygenated *p*-xylene were prepared at a concentration of 6.0×10^{-4} mol/L. A series of standards with varying concentration from 0 to 6.0×10^{-4} mol/L were prepared from these stock solutions and measured directly with UV−vis spectroscopy. The absorbance was measured at the maximum absorbance appearing at 390 nm for the Cu(I)Br/PPI complex and 380 nm for the Cu(I)Cl/PPI complex. The stability of the complexes in stock solutions was found to be good, as UV spectra remained unchanged over time for a period of several days. The presence of Cu(II) (maximum absorbance around 700 nm) could not be detected. Since the exchange reaction mixtures contained a large excess of hydroxy-TEMPO, which has a strong absorbance in the wavelength region where the catalyst concentrations are measured, identical exchange reactions with CuBr and CuCl were performed without the presence of hydroxy-TEMPO for UV−vis measurements. At timed intervals, the stirring of these reaction mixtures was temporarily stopped, and samples were withdrawn from the (homogeneous) top layer of the reaction mixture. The samples were diluted to a concentration of 2×10^{-4}−8×10^{-4} mol/L by adding weighed amounts to deoxygenated *p*-xylene and subsequently subjected to UV−vis spectroscopy.

Normal Phase Gradient Polymer Elution Chromatography (NP-GPEC). The GPEC analyses were performed using an Alliance Waters 2690 separation module, equipped with a Jordi Gel DVB polyamine column (250 × 4.6 mm) (Alltech) set at 35 °C. Solutions of 1−5 mg/mL of the purified polymer samples in dichloromethane were prepared, of which 10−30 μL was injected. A heptane−THF gradient was run from (100:0, v/v heptane:THF) to (0:100) in 25 min. The system was stepwise reset to initial conditions by pumping two column volumes of methanol, THF, and then dichloromethane, after which the column was reequilibrated in 30 min with heptane. Detection was done using a PL-EMD 960 ELSD detector (Polymer Laboratories). Data were acquired by Millennium 32 3.05 software.

Results and Discussion

The UV−vis calibration curves for the Cu(I)Br/PPI and Cu(I)Cl/PPI complexes are given in Figure 1. Apparently, the counterion has a strong effect on the absorption characteristics of the copper complex. Besides a shift in wavelength of maximum absorption from 390 nm for CuBr/PPI to 380 nm for CuCl/PPI, the extinction coefficient (ϵ) for CuBr/PPI is higher than for the CuCl/PPI complex (respectively 1840 and 930 L mol^{-1} cm^{-1}). Similarly, studies by Qiu et al.[17] indicate a strong influence of counterion and solvent polarity on the UV−vis absorption characteristics of copper-based complexes. To determine the actual concentration of Cu(I)Br/PPI and Cu(I)Cl/PPI during the exchange reactions, UV−vis spectrometric measurements of diluted reaction samples (without hydroxy-TEMPO) were performed. It is assumed that the hydroxy-TEMPO has little or no effect on the solubility of the copper complex. The results are shown in Figure 2, where the percentage of dissolved copper catalyst is plotted as a function of reaction time. Note that, after taking the sample at $t = 0$ min, the reaction mixture is immediately heated from room temperature to 90 °C, which accounts for the sudden increase in copper concentration during the first minutes.

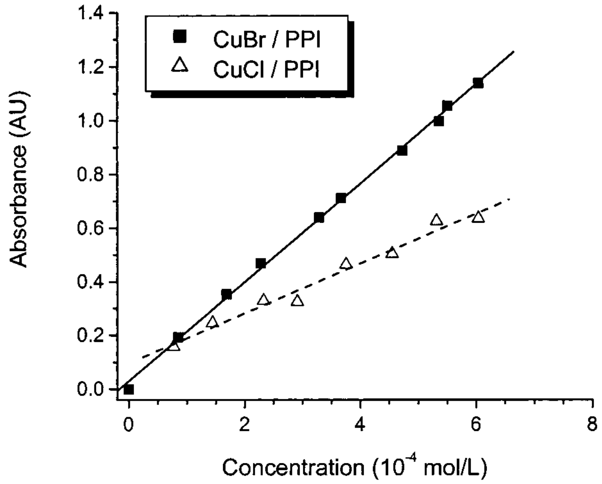


Figure 1. UV−vis calibration curves for Cu(I)Br/PPI (■ at 390 nm, $\epsilon = 1840$ L mol^{-1} cm^{-1}) and Cu(I)Cl/PPI (△ at 380 nm, $\epsilon = 930$ L mol^{-1} cm^{-1}) complexes in *p*-xylene.

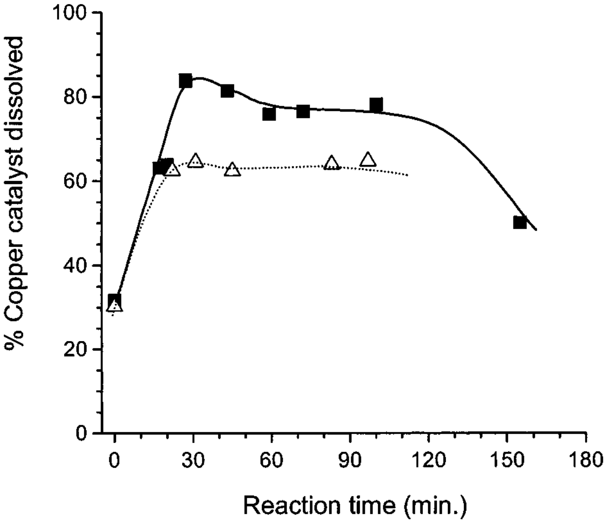


Figure 2. Concentration profile of the actual copper(I) concentration (in percentages of the recipe concentration) as a function of reaction time in the experiments without hydroxy-TEMPO for CuBr/PPI (■) and CuCl/PPI (△), as determined with UV−vis spectroscopy.

The results shown in Figure 2 indicate that, under the applied experimental conditions, only 65% of the CuCl is dissolved during the exchange reactions, whereas this is about 80% for the CuBr catalyst. Clearly, copper catalysts complexed by Schiff base ligands are less soluble in nonpolar solvents than those complexed by substituted bipyridines as a result of the higher polarity of the former. Determination of the copper(I) concentration is therefore of utmost importance. Note that despite their lower solubility, the Schiff base ligands are known to provide excellent control for the ATRP of methacrylate monomers, and their preparation is much easier than that of substituted bipyridines.[18] After reaching the equilibrium concentrations, the copper concentration only slightly decreases as the PEB−Br macroinitiator is activated since the ratio of catalyst to initiator is

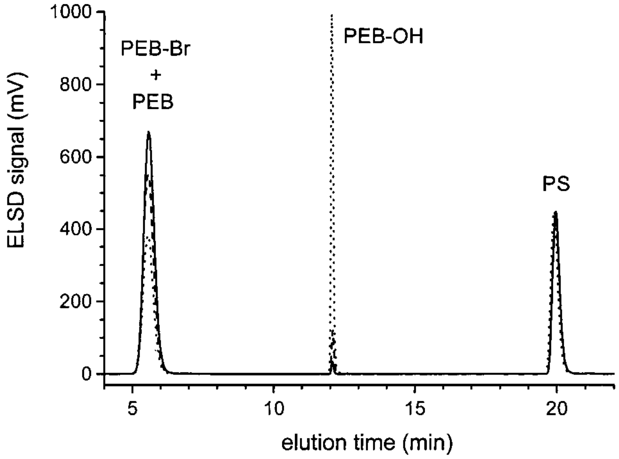


Figure 3. GPEC chromatograms of dried purified reaction samples taken before heating (—) (0 min reaction time) and after about 8 min (- - -) and 40 min (· · ·) reaction time. The chromatograms are normalized on the PS peak area of the sample at $t = 0$ min.

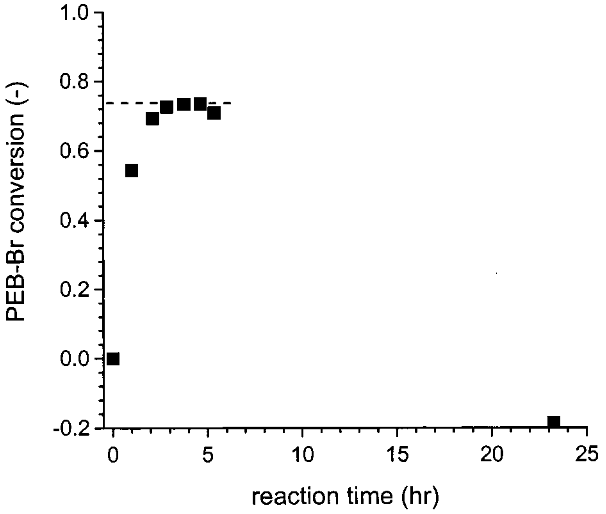


Figure 4. Macroinitiator (PEB−Br) conversion as a function of reaction time in the exchange experiments, as determined via GPEC.

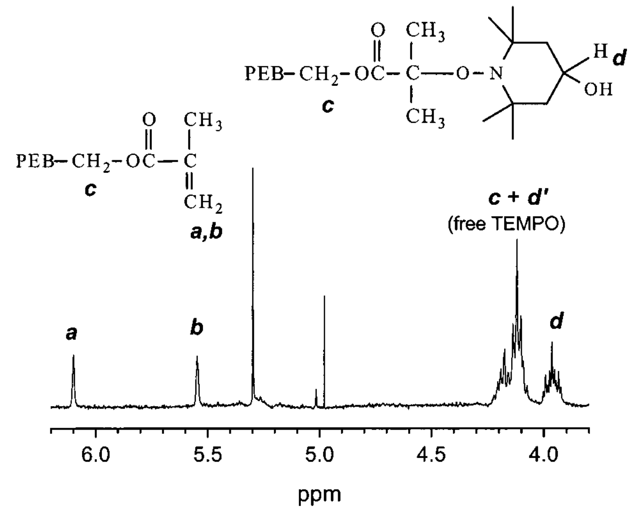


Figure 5. Partial ^{1}H NMR spectrum of a precipitated reaction sample at the maximum in PEB−Br conversion (5 h in Figure 4).

about 3 to 1. Moreover, in the absence of trapping agent, the activated species will be deactivated by Cu(II), resulting in regeneration of Cu(I). The rather fast decrease in concentration of the CuBr/PPI complex after 2 h is probably due to oxidation during sample preparation.

A typical evolution of the GPEC chromatograms of the purified polymer samples from the exchange reactions with increasing reaction time is shown in Figure 3. The residual PEB−Br elutes at about 5 min in pure heptane, whereas the trapped PEB−OH species elutes halfway the heptane−THF gradient due to its increased column interaction. For determining the amount of PEB−Br, all chromatograms were normalized on PS (internal standard) eluting at 20 min. To convert the ELSD signal into concentrations, calibration curves were constructed for the polymeric compounds (results given in Table 1) as the ELSD signal strongly depends on the mobile phase composition and scales to concentration with a power law.[19]

Calculation of k_{act} using eqs 2−4 requires knowledge on the fraction of activated chains that is terminated via combination, f_{tc}. To determine this fraction, a typical exchange reaction with Cu(I)Cl/PPI was conducted for longer reaction times while monitoring the area underneath the peak eluting at 5 min, which represents a mixture of the macroinitiator and the disproportionation product. Note that the amount of nonfunctional PEB−Br at the beginning of the exchange reactions is about 6%, of which $^2/_3$ is not esterified (PEB−OH) and only $^1/_3$ is non-hydroxyl-functional.[6] Figure 4 shows the appearance of a maximum of about 75% in PEB−Br conversion around 4 h, indicating that *25%* of the activated species is terminated via disproportionation. Complete activation of the macroinitiator chains at this time has been confirmed with ^{13}C NMR spectroscopy. After 4 h, the conversion of the macroinitiator decreases again, which is caused by the occurrence of disproportionation of the trapped (PEB−OH) product via decomposition (k_{dec} in Scheme 1) and/or via disproportionation after thermal dissociation (k_{td} and k_{d} in Scheme 1).

Figure 5 shows the ^{1}H NMR spectrum of a precipitated sample from the exchange experiment at the maximum in PEB−Br conversion (4−5 h, as shown in Figure 4). It is assessed that 22% of the PEB−Br chains is terminated via disproportionation with hydroxy-TEMPO, which is in excellent agreement with the GPEC analysis. After 1 day of reaction time, all trapped polymeric species are disproportionated (about 90% by ^{1}H NMR analysis). Though it is assumed here that the power law behavior of the PEB−Br species also applies to the disproportionation product as they both elute at the same time and only have a minor difference in end group, the negative PEB−Br conversion in Figure 4 may be a result of somewhat different parameters in the power law dependence. The amount of disproportionated PEB chains that is produced from the side reactions however strongly affects the position of the maximum in PEB−Br conversion shown in Figure 4. As the concentration of trapped species increases with time, the concentration of disproportionated chains increases as well, leading to a decrease in the observed value for f_{tc}. To determine a correct value for f_{tc}, the data in Figure 4 have been fitted using the Predici program with appropriate values for the various rate constants.[20] The effect of the side reactions on the ratio of termination via disproportionation and termination via trapping is displayed in Figure 6, where the apparent value for f_{tc}

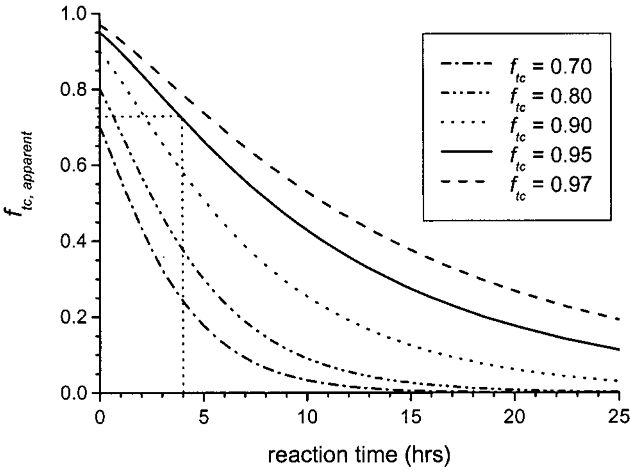


Figure 6. Apparent fraction of activated PEB−Br chains that are terminated via combination with hydroxy-TEMPO ($f_{tc,\ apparent}$ is calculated by the ratio of concentration profiles: [P−OH]/([P−OH] + [P=])) as a function of reaction time for different f_{tc} values used in the Predici simulations.[20]

as a function of reaction time is simulated for different entry values of f_{tc}. The apparent value for f_{tc} strongly decreases with increasing reaction time. According to the simulations in Figure 6, the maximum of 75% PEB−Br conversion (i.e., $f_{tc} = 0.75$) at 4 h (Figure 4) corresponds to an intrinsic f_{tc} of 0.95. As the activation rate parameter is calculated from the data obtained within the first hour of reaction time, it is justifiable to assume a constant value for f_{tc} since in this period of time the deviation of this value is less than 5%, as shown in Figure 6. Indeed, the activated bromoisobutyrate group and its adduct with hydroxy-TEMPO are found to be much more susceptible to side reactions as thermal dissociation and decomposition than polystyrene−TEMPO adducts.[21,22] Accurate determination of the activation rate parameter in ATRP for methacrylic initiating species therefore requires detailed knowledge on the relevance of side reactions occurring, which may be system dependent.

The pseudo-first-order plots for the exchange reaction of PEB−Br catalyzed by CuBr/PPI and CuCl/PPI in xylene at 90 °C are calculated from eqs 2 and 3, where the residual concentration of PEB−Br is calculated using eq 4 with $f_{tc} = 0.95$. The results are given in Figure 7, where (ln A + ln B)/C is plotted as a function of time. Another potential source of error on the value of k_{act} is the purity of the catalyst employed. In Table 2 the k_{act} values are listed for the Cu(I)Br/PPI and Cu(I)-Cl/PPI catalyzed exchange reactions, in which catalysts of different purity are used. Note that the catalyst is not fully dissolved during the exchange experiments. Variations in the catalyst concentration within the series of experiments are therefore likely to occur, which makes it under these circumstances practically impossible to quantify any effects of catalyst purity on k_{act}.

The activation rate parameters are of the same order of magnitude as those for bromide functional poly(butyl acrylate) with CuBr/dHbpy at 110 °C (about 0.07 L mol^{-1} s^{-1})[11] and for 1-phenylethyl chloride with CuCl and CuBr/dHbpy at 110 °C (respectively 0.018 and 0.010 L mol^{-1} s^{-1}).[10] Clearly, the ligand influences the activation rate parameter to a large extent through affecting the redox potential of the copper(I) complexes. The presence of chloride as copper counterion results in a strong increase in the activation rate parameter by a factor of almost 3, compared to bromide as counterion (0.038 L mol^{-1} s^{-1} for CuCl/PPI and 0.014 L mol^{-1} s^{-1} for CuBr/PPI, within 10% error[23]). This trend is consistent with the results reported by Goto and Fukuda[10] and clearly demonstrates that the improved control of the molecular weight and molecular weight distribution for mixed halide systems as R−Br/CuCl is not entirely based on an increased ratio of initiation to propagation rate through halogen exchange, as explained by Matyjaszewski et al.,[7] but also results from chloride as the copper counterion having a positive effect on the rate of activation of initiating species. The extent to which the counterion affects the activation rate parameter in ATRP might be dependent on the type of ligand and/or initiator that is applied.

Most probably, the effect of the copper counterion on the activation rate parameter finds its origin in its effect on the position of the metal to ligand charge transfer

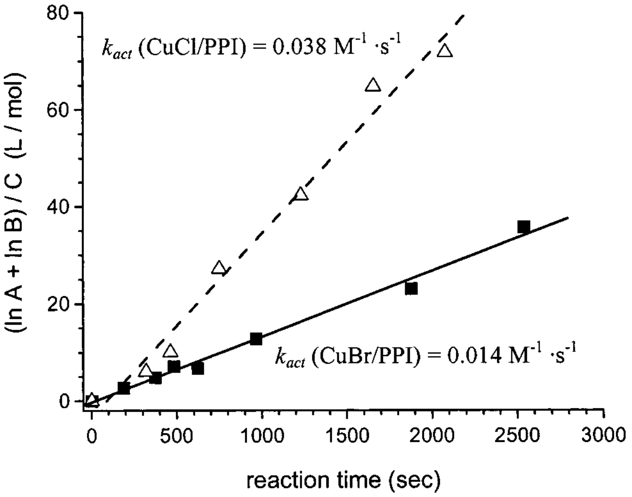


Figure 7. Pseudo-first-order plots for the exchange reactions of PEB−Br catalyzed by CuBr/PPI (■) and CuCl/PPI (△). On the y-axis: $A = ([\text{P−Br}]_0/[\text{P−Br}]_t)$, $B = \{([\text{Cu(I)}]_0 - [\text{P−Br}]_0 + [\text{P−Br}]_t)/[\text{Cu(I)}]_0\}$, and $C = [\text{Cu(I)}]_0 - [\text{P−Br}]_0$. Plots are calculated with $f_{tc} = 0.95$, and $[\text{Cu(I)Br}]_0$ and $[\text{Cu(I)Cl}]_0$ are 0.80 and 0.65 times the recipe concentration, respectively.

Table 1. Calibration Curves for ELSD Quantification in GPEC Analyses

	peak area = aC^b		
polymeric species	a	b	regression coeff
PEB−Br	105	1.78	0.9994
PEB−OH[a]	220	1.44	0.9994
PS	256	1.58	0.9991

[a] As the trapped PEB species is not available as pure component, the PEB−OH (Kraton L-1203) precursor of the PEB−Br macroinitiator, which elutes at the same time, is used.

Table 2. Values for the Activation Rate Parameter for PEB−Br (Having an Isobutyryl Bromide Functional Group) at 90 °C in *p*-Xylene for CuBr and CuCl Catalysts

exchange expt	catalyst system	purity (%)[a]	k_{act} (L mol^{-1} s^{-1})[b]
1	CuBr/PPI	98	0.017
2	CuBr/PPI	99.999	0.014
3	CuCl/PPI	99+	0.038
4[c]	CuCl/PPI	99+	0.040
5[d]	CuCl/PPI	99.995+	0.031

[a] Maximum values are given as determined by Aldrich Chemical Co. [b] Values obtained from linear fits of pseudo-first-order data points are within error of 5−10%. [c] Duplicate of exchange experiment 3. [d] Error of fit 10−15%.

(MLCT) band through π-back-bonding interactions. For copper(I) complexes with 4-monosubstituted pyridines it has been reported that the difference in energy between the t_2 and the lowest vacant π^* orbitals of pyridine increases in the order of Cl < Br < I.[24] Thus, replacement of Br with Cl as copper counterion leads to a decreased stability of the t_2 orbital. It remains however unclear how and if this decreased orbital stability influences the rate of activation. Obviously, additional research is required to determine the mechanistic background of the effect of the copper counterion on the activation rate parameter.

Conclusions

It was demonstrated that the copper counterion has a strong effect on the activation rate parameter (k_{act}) in ATRP. When compared to bromide, the application of chloride as copper counterion clearly results in an increased rate of activation of initiating species. The improved control of ATRP for mixed halide systems as R−Br/CuCl is therefore not entirely based on an increased ratio of initiation to propagation rate through halogen exchange but also results from the positive effect of chloride as counterion on the activation rate parameter. Values for k_{act} for a poly(ethylene-*co*-butylene) (PEB) macroinitiator bearing a bromoisobutyryl (MMA-like) initiating group with *N*-*n*-pentyl-2-pyridylmethanimine (PPI) ligated CuBr and CuCl in *p*-xylene at 90 °C have been determined at 0.038 L mol^{-1} s^{-1} for CuCl/PPI and 0.014 L mol^{-1} s^{-1} for CuBr/PPI. It has been shown that the use of a macroinitiator for nitroxide exchange experiments in combination with GPEC provides the possibility to perform an accurate determination of the activation rate parameter in ATRP, provided that the copper concentrations are known. Furthermore, GPEC is a powerful tool to determine the amount of side products that are generated during the nitroxide exchange experiments, which is detrimental for MMA-like initiators, since a large portion is terminated via disproportionation through dissociation and decomposition of the trapped species.

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(20) The data from the exchange experiment with CuCl/PPI given in Figure 4 have been fitted using the following rate constants (definitions are given in Scheme 1): $k_{\mathrm{act}} = 0.04$ L mol^{-1} s^{-1} (this work), $k_{\mathrm{deact}} \approx 10^7$ L mol^{-1} s^{-1} (see e.g.: Ohno, K.; Goto, A.; Fukuda, T.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 2699) and the termination rate coefficient (for $2\mathrm{P}^\bullet \rightarrow \mathrm{D}$) $k_{\mathrm{t}} \approx 10^7$ L mol^{-1} s^{-1} (for initial chain length of about 100, De Kock, J. B. L. Ph.D. Thesis, Technische Universiteit Eindhoven, Eindhoven, 1999). Rate constants for dissociation and decomposition of PMMA−TEMPO adducts are not known. Though not entirely correct, the rate constants reported for *tert*-butyl methacrylate−TEMPO adducts were used in the simulations: $k_{\mathrm{d}} = 3 \times 10^{-4}$ s^{-1} (Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. *Macromolecules* **2000**, *33*, 4403) and $k_{\mathrm{dec}} = 10^{-5}$ s^{-1} (Fukuda, T., personal communication), both at 80 °C. The rate constants for dissociation and decomposition of *t*BMA−TEMPO adducts at 80 °C were found to fit the data in Figure 4 with reasonable accuracy, even though the exchange experiment was conducted at 90 °C. Possibly, the *tert*-butyl group exerts a destabilizing effect on the adduct, thereby increasing k_{d} and k_{dec} compared to those of MMA−TEMPO adducts. Furthermore, using these data, the best fit was obtained with $k_{\mathrm{tc}} \approx 9.5 \times 10^7$ L mol^{-1} s^{-1} and $k_{\mathrm{td}} \approx 5 \times 10^6$ L mol^{-1} s^{-1}, i.e. $f_{\mathrm{tc}} = 0.95$ (for trapping rate constants, see e.g.: Bowry, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992). Note that this value for f_{tc} is within 5% error when taken into account a 50% error in the reported values for k_{d} and k_{dec}. The concentrations in the exchange experiment were as follows: $[\mathrm{P{-}Br}]_0 = 4.30 \times 10^{-3}$ mol L^{-1}, $[\mathrm{Cu}^+]_0 = 8.78 \times 10^{-3}$ mol L^{-1} (65% of the Cu(I)Cl recipe concentration), $[\mathrm{TEMPO{-}OH}]_0 = 9.14 \times 10^{-2}$ mol L^{-1}, and zero initial concentrations of Cu^{2+}, $\mathrm{P}^\bullet$, P=, and P−OH.

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(23) The errors that are made in determining the fraction of activated PEB−Br chains terminated by combination with hydroxy-TEMPO and the percentage of copper(I) dissolved are each estimated to be less than 5%. With these errors, the calculated values for the activation rate parameter are within 10% error. Note that higher errors of about 15% are obtained in the situation that both f_{tc} and the percentage of copper(I) dissolved are simultaneously under- or overestimated by 5%.

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