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Determination of ATRP Equilibrium Constants under Polymerization Conditions

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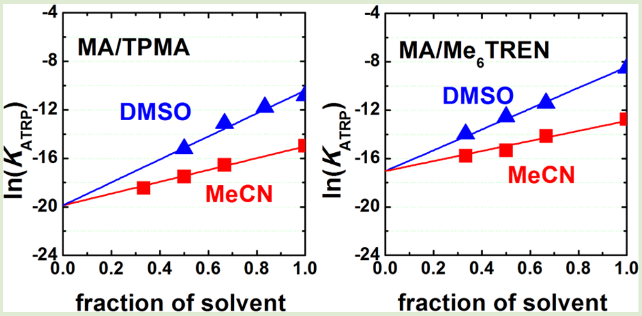
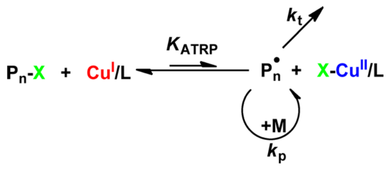
Supporting Information

ABSTRACT: Atom transfer radical polymerization (ATRP) equilibrium constants (K_{ATRP}) were measured during polymerization of methyl acrylate (MA) with $Cu^IBr/Cu^{II}Br_2$ in either dimethyl sulfoxide (DMSO) or acetonitrile (MeCN) in the presence of either tris(2-pyridylmethyl)amine (TPMA) or tris[2-(dimethylamino)ethyl]amine (Me_6TREN) as the ligand and with ethyl 2-bromopropionate as the initiator. The ln(K_{ATRP}) values changed linearly with the volume fraction of solvents in the reaction medium, allowing extrapolation of the values for K_{ATRP} to bulk conditions, which were 2×10^{-9} and 3×10^{-8} for TPMA and Me_6TREN ligands at 25 °C, respectively. The temperature effect on K_{ATRP} values was studied in MA/MeCN = 1/1 (v/v) with TPMA as the ligand in the temperature range from 0 to 60 °C. The K_{ATRP} values increased with temperature providing ΔH = 36 kJ mol^{-1} in MeCN.



Atom transfer radical polymerization (ATRP)[1−4] can be conducted with a range of transition metal complexes, such as Cu, Ru, Fe, Ni, Os, and so on,[5−8] as catalysts. It is one of the most widely used controlled/living radical polymerization (CRP)[9] techniques. ATRP provides access to well-defined homopolymers and designed copolymers as well as materials with complex architectures, including block copolymers, stars, and brushes.[10,11] In the predominantly practiced ATRP process, the radicals are formed by Cu^I/L catalyzed activation of an alkyl halide and control is provided via rapid deactivation of the radical by the formed, or added, $X\text{-}Cu^{II}/L$ catalyst complex. This process of repetitive activation/deactivation is defined by an equilibrium constant K_{ATRP} as shown in Scheme 1. In a well-controlled ATRP, the equilibrium is strongly shifted to the dormant alkyl halide side by the presence of the $X\text{-}Cu^{II}/L$ complex, which acts as the "persistent radical".[12] One limitation of a normal ATRP, initially conducted with a lower activity catalyst complex, was that a relatively large amount of the Cu^I/L activator was added to the reaction in order to sustain a reasonable polymerization rate and overcome the buildup of $X\text{-}Cu^{II}/L$ deactivator caused by termination reactions.[13] Improved ATRP methods, based on higher activity catalyst complexes, were developed allowing well controlled polymerizations to be conducted with ppm level of Cu catalyst including activators regeneration by electron transfer (ARGET),[14,15] initiators for continuous activator regeneration (ICAR),[16] supplemental activators and reducing agents (SARA),[6,17−24] electrochemically mediated ATRP (*e*ATRP),[25] and photochemically mediated ATRP.[26−30]

Scheme 1. ATRP Equilibrium, where P_n-X is an Alkyl Halide (Macro)initiator, Cu^I/L is the Activator Complex, $P_n^{\bullet}$ is a (Macro)radical, and $X\text{-}Cu^{II}/L$ is the Deactivator Complex



The K_{ATRP} values for catalysts formed with various ligands and a range of alkyl halides were systematically studied in acetonitrile (MeCN)[31,32] and the effect of different solvents on K_{ATRP} was later reported.[33] Solvents have significant influence on K_{ATRP} values. For example, for the reaction of methyl α-bromoisobutyrate (MBiB) with Cu^IBr/HMTETA (HMTETA: 1,1,4,7,10,10-hexamethyltriethylenetetramine) the value of $K_{ATRP} = 3.1 \times 10^{-9}$ has been reported in pure acetone but for the same reaction in pure dimethyl sulfoxide (DMSO) $K_{ATRP} = 2.6 \times 10^{-7}$, which is ~$10^2$ times larger than that in acetone.[33] In an actual polymerization system, the reaction medium is initially a mixture of solvent/monomer, which gradually changes to solvent/monomer/polymer with increasing fraction of polymers. Thus, the values of K_{ATRP} measured in

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pure solvents could not be directly applied to real polymerization systems. In this paper, we report the measurement of K_{ATRP} under polymerization conditions and the correlation between the K_{ATRP} values and the volume fraction of solvent present in the reaction medium.

Values of K_{ATRP} were first measured for the polymerization of methyl acrylate (MA) in MeCN with $\mathrm{Cu^IBr}$/TPMA as the catalyst (TPMA: tris(2-pyridylmethyl)amine). A relatively slow polymerization was observed in the presence of initially added $\mathrm{Cu^{II}Br_2}$/L. Because the concentration of radical, $[\mathrm{P}_n^\bullet]$, was low, the rate of termination was also small, and the ratio $[\mathrm{Cu^I/L}]/[\mathrm{X\text{-}Cu^{II}/L}]$ did not change significantly during the measurement because the increase of $[\mathrm{X\text{-}Cu^{II}/L}]$ resulted only from the relatively slow termination. The amount of in situ formed $\mathrm{Cu^{II}}$ species was significantly smaller than $\mathrm{Cu^{II}}$ initially added and the contribution of the persistent radical effect (PRE) was very small. Consequently, linear first order kinetics was observed, and K_{ATRP} could be calculated via eq 2,[34]

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{P}_n^\bullet] = k_{\mathrm{p}}[\mathrm{M}]K_{\mathrm{ATRP}}[P_n\text{-X}]\frac{[\mathrm{Cu^I/L}]}{[\mathrm{X\text{-}Cu^{II}/L}]} \tag{1}$$

$$K_{\mathrm{ATRP}} = -\frac{[\mathrm{X\text{-}Cu^{II}/L}]}{k_{\mathrm{p}}[\mathrm{P_n\text{-}X}][\mathrm{Cu^I/L}]}\frac{\mathrm{d}\ \ln[\mathrm{M}]}{\mathrm{d}t} \tag{2}$$

where $-\mathrm{d}\ \ln[\mathrm{M}]/\mathrm{d}t$ is the slope of the plot of $\ln([\mathrm{M}]_0/[\mathrm{M}])$ versus t.

The polymerization of MA was performed in MA/MeCN = 1/1 (v/v) with the ratio of reagents: $[\mathrm{MA}]:[\mathrm{EBrP}]:[\mathrm{Cu^IBr}]:[\mathrm{Cu^{II}Br_2}]:[\mathrm{TPMA}] = 200:1:0.2:0.2:0.24$, with $[\mathrm{EBrP}] = 0.028$ M, at 25 °C (EBrP: ethyl 2-bromopropionate). The conversion of monomer was determined via UV/vis/NIR from the integration of the signal between $\lambda = 1610$ to 1625 nm originating from the first C−H stretching overtone at the C═C double bond. The concentration of $\mathrm{X\text{-}Cu^{II}/L}$ was monitored from the UV/vis/NIR absorption at $\lambda = 960$ nm, see, Supporting Information (SI). After 2 h, the $[\mathrm{Cu^I/L}]/[\mathrm{X\text{-}Cu^{II}/L}]$ ratio changed from 1.0 to 0.94, when the conversion of monomer reached 6.5%. Thus, the uncertainty in the calculated values of K_{ATRP} due to the change of $[\mathrm{Cu^I/L}]/[\mathrm{X\text{-}Cu^{II}/L}]$ was ~5%. The increase of $[\mathrm{Cu^{II}}]$ was 0.15 mM and this corresponds to a decrease of $[\mathrm{P_n\text{-}X}]$ by only 0.56%, because $[\mathrm{R\text{-}X}]_0 = 27.8$ mM.[13] The value of $-\mathrm{d}\ \ln[\mathrm{M}]/\mathrm{d}t$ obtained by linear fitting of the first order kinetic plots of monomer conversion was $1.0 \times 10^{-5}\ \mathrm{s^{-1}}$. The value of radical propagation for MA was taken as $k_{\mathrm{p}} = 8.1 \times 10^3$, 1.6×10^4, 2.2×10^4, and $3.3 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ at 0, 25, 40, and 60 °C based on the literature data.[35] The k_{p} values vary slightly in conventional organic solvents.[36] The possible solvent effect on the k_{p} values could contribute only ~15%, see SI. Consequently, K_{ATRP} was calculated as 2.2×10^{-8} at 25 °C. This reaction was repeated three times with various amounts of Cu catalyst and the results are reported in Figure 1.

The K_{ATRP} values were calculated to be 2.2×10^{-8}, 2.7×10^{-8}, and 2.5×10^{-8} for 0.2, 0.1, and 0.05 equiv $\mathrm{Cu^IBr}$ (or $\mathrm{Cu^{II}Br_2}$) to EBrP, respectively, providing an average value of $K_{\mathrm{ATRP}} = 2.5 \times 10^{-8}$. This value can be compared to the literature value for K_{ATRP} for the model reaction between methyl 2-bromopropionate (MBrP) and $\mathrm{Cu^IBr}$/TPMA in pure MeCN of 3.2×10^{-7}.[32] The value determined for a 1/1 (v/v) mixture of MeCN/MA, which changes gradually to MeCN/MA/PMA-Br was 13 times smaller than in pure MeCN.

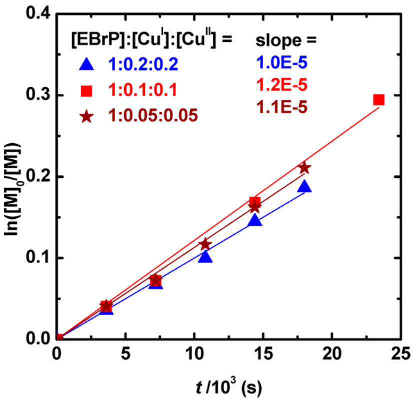

Figure 1. Kinetic plots of $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs t for ATRP of MA in MA/MeCN = 1/1 (v/v) at 25 °C with the ratio of reagents $[\mathrm{MA}]:[\mathrm{EBrP}]:[\mathrm{Cu^IBr}]:[\mathrm{Cu^{II}Br_2}]:[\mathrm{TPMA}] = 200:1:X:X:1.2X$, where $X = 0.2$, 0.1, and 0.05, respectively.

Therefore, a significant error would have been involved, if the K_{ATRP} value obtained in pure solvent would be applied to analyze kinetics of the real polymerization system. The differences in K_{ATRP} values determined in polymerization of styrene (St) or methyl methacrylate (MMA) and in model study was previously reported.[37] These differences could originate in both medium effects and intrinsic reactivities of macromolecular and low molar mass species.

The K_{ATRP} values for $\mathrm{Cu^IBr}$/TPMA and $\mathrm{Cu^IBr/Me_6TREN}$ in MeCN and DMSO with different volume fractions of solvent were determined. Because the activity of $\mathrm{Cu^IBr}$/TPMA and $\mathrm{Cu^IBr/Me_6TREN}$ in DMSO were so high, reliable values could not be measured following the conventional spectroscopic techniques,[31] and therefore, stopped flow was employed to determine K_{ATRP}. Using the modified PRE method, as reported by Tang et al.,[31] values of 2.0×10^{-5} for $\mathrm{Cu^IBr}$/TPMA and 2.0×10^{-4} for $\mathrm{Cu^IBr/Me_6TREN}$ were determined in pure DMSO at 25 °C. They can be compared to the value $K_{\mathrm{ATRP}} = 2.9 \times 10^{-6}$ for $\mathrm{Cu^IBr/Me_6TREN}$ in pure MeCN.[32]

ATRP of MA was performed in MeCN and DMSO, with TPMA and $\mathrm{Me_6TREN}$ as the ligand to determine K_{ATRP} values. The solvent effect on k_{p} values in DMSO might be larger than that in MeCN because the polarity of DMSO is higher. In 50% (v/v) DMSO, the k_{p} value for MMA increases ~70%, as compared to bulk, see SI. Assuming that solvent has the same influence on the k_{p} values for MA and MMA, the calculated K_{ATRP} values could be affected to a similar degree. Nevertheless, the solvent effect on k_{p} values is much smaller than on K_{ATRP} values, see Figure 2. In all cases, $\ln(K_{\mathrm{ATRP}})$ values changed linearly with the volume fraction of solvent. The K_{ATRP} values of $\mathrm{Cu^IBr}$/TPMA and $\mathrm{Cu^IBr/Me_6TREN}$ in bulk were calculated to be $K_{\mathrm{ATRP}} = 2 \times 10^{-9}$ and 3×10^{-8} at 25 °C, which were difficult to measure directly due to the poor solubility of the $\mathrm{Cu^{II}}$ species in bulk methyl acrylate.

The linear correlation between $\ln(K_{\mathrm{ATRP}})$ and the volume fraction of solvent indicates that the measurements based on polymerization kinetics at known $[\mathrm{Cu^I/L}]/[\mathrm{X\text{-}Cu^{II}/L}]$ ratios and those using modified PRE[31,32] provide similar values of K_{ATRP}. This also indicates that K_{ATRP} for macromolecular PMA-Br and a model, low molar mass, MBrP are similar.

For both TPMA and $\mathrm{Me_6TREN}$, the scaling from the bulk condition to solvents gave very similar trends. In pure MeCN the K_{ATRP} values are ~10^2 larger than that in bulk; while the K_{ATRP} values increase by a factor of nearly 10^4 as one transitions

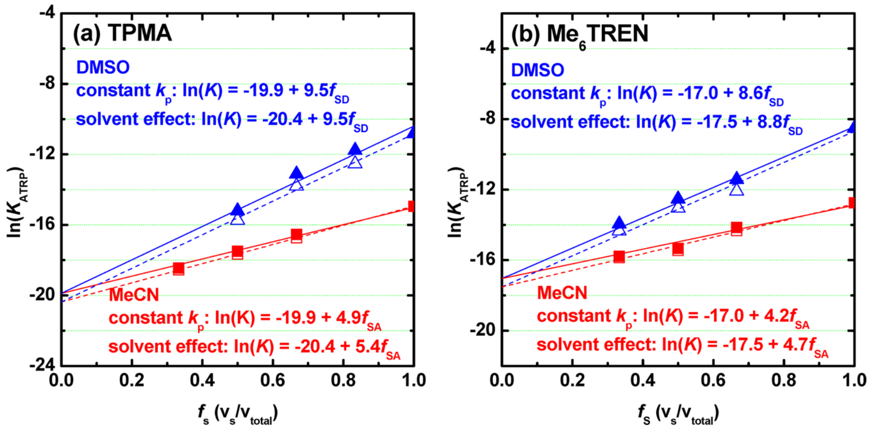

Figure 2. Plots of ln(K_{ATRP}) values for ATRP of MA vs the volume fraction of solvent (f_S) with (a) TPMA and (b) Me_6TREN as the ligand, in MeCN or DMSO at 25 °C. Solid dots are experimental data calculated by assuming constant k_p values; hollow dots are calculated considering solvent effect on k_p. Solid lines are linear fitting of experimental results assuming constant k_p values; dash lines are linear fitting of the experimental data considering solvent effect on k_p. The equation used for the least-squares fitting is $\ln(K) = a + b \times f_{SA} + c \times f_{SD}$, where f_{SA} is the volume fraction of MeCN and f_{SD} is that of DMSO.

from bulk to pure DMSO. Obviously, the K_{ATRP} value in pure MeCN or DMSO should not be used directly for evaluation of the ATRP under bulk conditions. The K_{ATRP} values for both TPMA and Me_6TREN in pure DMSO are ca. 100 times larger than in pure MeCN. A correlation between volume fraction of the solvent and ln(K_{ATRP}) could allow for additional solvent-induced tuning of ATRP rates and equilibria.

The values of K_{ATRP} were measured during the polymerization of MA at 0, 25, 40, and 60 °C in MeCN with 50% (v/v) solvent with TPMA as the ligand, and the results are reported in Figure 3. The K_{ATRP} values increased from 7×10^{-9} at 0 °C to 1×10^{-7} at 60 °C. The ΔH value could be calculated as 36 kJ mol^{-1} by plotting of ln(K_{ATRP}) versus 1/T. Comparing the reported ΔH values for ATRP of St with different ligands, a general trend could be observed that less active system has higher ΔH.[34,37] However, more detailed study is required in order to get deeper understanding of the temperature effect on ATRP equilibrium.

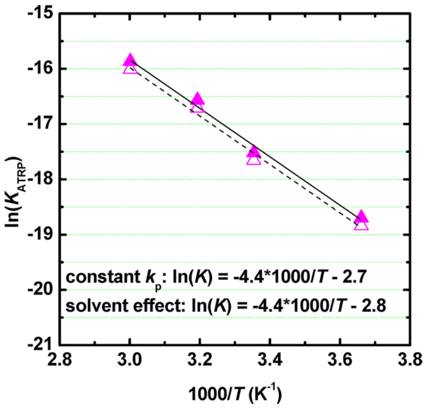

Figure 3. Linear correlation between ln(K_{ATRP}) and 1/T for ATRP of MA at 0, 25, 40, and 60 °C in 50% (v/v) MeCN with TPMA as the ligand. Solid points represent the average of experimental values calculated by assuming constant k_p values; hollow dots are calculated considering possible solvent effect on k_p. Solid line is linear fitting of experimental data assuming constant k_p values; dash line is linear fitting of the experimental data considering possible solvent effect. ΔH was calculated as 36 kJ mol^{-1}.

In summary, K_{ATRP} values were measured at different solvent/monomer ratios for ATRP of MA with TPMA or Me_6TREN as the ligand in MeCN or DMSO. A linear correlation between ln(K_{ATRP}) values and the volume fraction of solvent was found. The K_{ATRP} values for Br/Cu species were extrapolated to 2×10^{-9} and 3×10^{-8} for TPMA and Me_6TREN in bulk at 25 °C, respectively. In a reaction mixture with 50% (v/v) MeCN, the K_{ATRP} values were measured at different temperatures, providing ΔH = 36 kJ mol^{-1} in the temperature range from 0 to 60 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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