---Supporting Information---

Solvent Effects on the Activation Rate Constant in Atom Transfer Radical Polymerization

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Activation Rate Constants

Similar to the case in acetonitrile, CuBr and $Cu(CH_3CN)_4BF_4$ as catalyst precursors gave identical activation rate constants in DMSO (Figure S1).

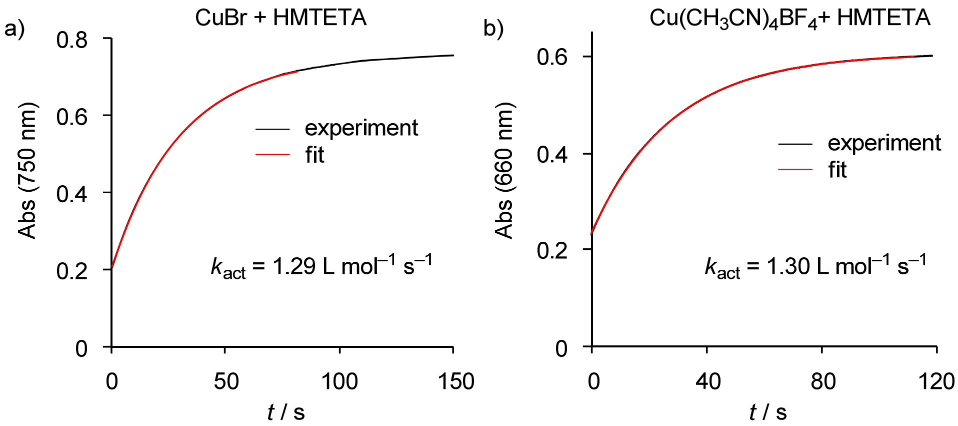


Figure S1. Exponential increase of the absorbances during the reactions of EBiB with $[Cu^I/HMTETA]^+$ in DMSO at 25 °C, [EBiB] = 26.7 mM, [TEMPO] = 30.0 mM; a) using CuBr as catalyst precursor, [CuBr] = 2.93 mM, [HMTETA] = 2.94 mM; b) using $Cu(CH_3CN)_4BF_4$ as catalyst precursor, $[Cu(CH_3CN)_4BF_4]$ = 2.92 mM, [HMTETA] = 3.01 mM.

Doubling the initiator concentration $[EBiB]_0$ in DMSO increased the observed rate constant k_{obs} by a factor of 2 (Figure S2). Other expamples are liste in Tables S1 and S2. This proves the operation of a second-order rate law for the activation step.

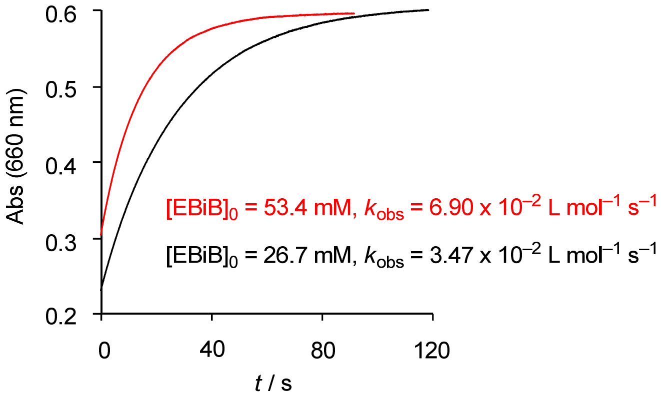


Figure S2. Exponential increase of the absorbance during the reactions of EBiB with $[Cu^I/HMTETA]^+$ in DMSO at 25 °C, $[Cu(CH_3CN)_4BF_4]$ = 2.92 mM, [HMTETA] = 3.01 mM, [TEMPO] = 30.0 mM.

Table S1. Summary of all Rate Constants using CuBr as Catalyst Precursor, HMTETA as Ligand L, and EBiB as Initiator I, 25 °C.

Solvent	$[I]_0$ /mM	$[CuBr]_0$ /mM	$[L]_0$ /mM	$[TEMPO]_0$ /mM	k_{obs} /s^{-1}	k_{act} /M^{-1} s^{-1}	Average /M^{-1} s^{-1}
Anisole	27.1	2.93	2.94	30.0	2.04×10^{-3}	7.53×10^{-2}	$\mathbf{7.38 \times 10^{-2}}$
	27.1	2.93	2.94	60.0	1.98×10^{-3}	7.31×10^{-2}	
	54.1	2.93	2.94	30.0	4.09×10^{-3}	7.56×10^{-2}	
	54.1	2.93	2.94	60.0	3.84×10^{-3}	7.10×10^{-2}	
Acetonitrile	27.1	2.93	2.94	30.0	1.66×10^{-3}	6.13×10^{-2}	$\mathbf{6.06 \times 10^{-2}}$
	27.1	2.93	2.94	30.0	1.74×10^{-3}	6.42×10^{-2}	
	54.1	2.93	2.94	30.0	3.08×10^{-3}	5.69×10^{-2}	
	54.1	2.93	2.94	30.0	3.25×10^{-3}	6.01×10^{-2}	
Acetone	26.7	3.07	3.09	30.0	1.36×10^{-3}	5.09×10^{-2}	$\mathbf{5.05 \times 10^{-2}}$
	53.4	3.07	3.09	30.0	2.67×10^{-3}	5.00×10^{-2}	
Butanone	27.1	2.93	2.94	30.0	1.12×10^{-3}	4.13×10^{-2}	$\mathbf{4.17 \times 10^{-2}}$
	54.1	2.93	2.94	30.0	2.28×10^{-3}	4.21×10^{-2}	
DMSO	27.1	2.93	2.94	30.0	3.58×10^{-2}	1.32	**1.29**
	26.7	2.93	2.94	30.0	3.66×10^{-2}	1.25	
DMF	26.5	2.93	2.94	30.0	6.85×10^{-3}	$\mathbf{2.58 \times 10^{-1}}$	**-**
DMA	27.1	2.93	2.94	30.0	3.85×10^{-3}	1.42×10^{-1}	$\mathbf{1.33 \times 10^{-1}}$
	54.1	2.93	2.94	30.0	6.95×10^{-3}	1.28×10^{-1}	
	54.1	5.86	5.88	30.0	6.90×10^{-3}	1.28×10^{-1}	
Formamide	27.1	2.93	2.94	30.0	2.27×10^{-2}	8.38×10^{-1}	$\mathbf{8.39 \times 10^{-1}}$
	54.1	2.93	2.94	30.0	4.54×10^{-2}	8.39×10^{-1}	
NMP [a]	2.00	2.00	2.00	20.0	-	2.85×10^{-1}	$\mathbf{2.73 \times 10^{-1}}$
	5.00	5.00	5.00	20.0	-	2.61×10^{-1}	
PC [a]	2.00	2.00	2.00	20.0	-	1.21×10^{-1}	$\mathbf{1.12 \times 10^{-1}}$
	2.00	2.00	2.00	20.0	-	1.03×10^{-1}	
MeOH	27.1	2.93	2.94	30.0	2.86×10^{-3}	1.06×10^{-1}	$\mathbf{1.11 \times 10^{-1}}$
	54.1	2.93	2.94	30.0	5.93×10^{-3}	1.10×10^{-1}	
	27.1	2.93	2.94	30.0	3.02×10^{-3}	1.11×10^{-1}	
	54.1	2.93	2.94	30.0	6.20×10^{-3}	1.15×10^{-1}	
EtOH	27.1	2.93	2.94	30.0	7.42×10^{-3}	2.74×10^{-1}	$\mathbf{2.24 \times 10^{-1}}$
	27.1	2.93	4.41	30.0	7.12×10^{-3}	2.63×10^{-1}	
	27.1	2.93	5.88	30.0	5.29×10^{-3}	1.95×10^{-1}	
	27.1	2.93	2.94	60.0	4.95×10^{-3}	1.83×10^{-1}	
	54.1	2.93	2.94	60.0	1.10×10^{-2}	2.03×10^{-1}	
2-PrOH	27.9	2.93	2.94	30.0	3.90×10^{-3}	1.40×10^{-1}	$\mathbf{1.38 \times 10^{-1}}$
	54.1	2.93	2.94	30.0	7.30×10^{-3}	1.35×10^{-1}	
2,2,2-TFE	27.1	2.93	2.94	30.0	1.94×10^{-3}	7.16×10^{-2}	$\mathbf{6.84 \times 10^{-2}}$
	54.1	2.93	2.94	30.0	3.53×10^{-3}	6.52×10^{-2}	

[a] Methyl α-bromoisobutyrate (MBiB) was used as initiator; equimolar amounts of I and C were used.

Table S2. Summary of all Rate Constants using $Cu(CH_3CN)_4BF_4$ as Catalyst Precursor, HMTETA as Ligand L, and EBiB as Initiator I, 25 °C.

Solvent	$[I]_0$ /mM	$[Cu]_0$ /mM	$[L]_0$ /mM	$[TEMPO]_0$ /mM	k_{obs} /s^{-1}	k_{act} /M^{-1} s^{-1}	Average /M^{-1} s^{-1}
Acetone	26.7	2.92	3.01	30.0	1.16×10^{-3}	**4.34×10^{-2}**	
Acetonitrile	26.7	2.92	3.01	30.0	1.59×10^{-3}	5.96×10^{-2}	**5.82×10^{-2}**
Acetonitrile	53.4	2.92	3.01	30.0	3.03×10^{-3}	5.67×10^{-2}	
DMSO	26.7	2.92	3.01	30.0	3.47×10^{-2}	1.30	**1.30**
DMSO	53.4	2.92	3.01	30.0	6.90×10^{-2}	1.29	

Table S3. Summary of Activation Rate Constants in Mixtures of Methyl Esters with DMSO or DMF, 25 °C.

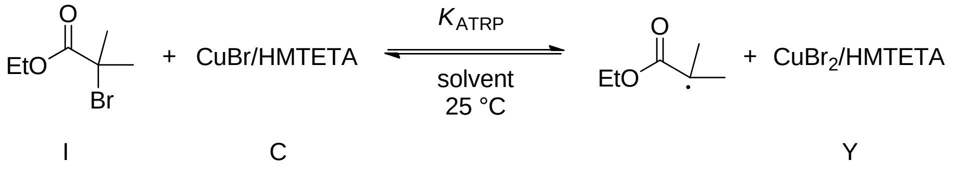
Solvent	$[I]_0$ /mM	$[CuBr]_0$ /mM	$[L]_0$ /mM	$[TEMPO]_0$ /mM	k_{obs} /s^{-1}	k_{act} /M^{-1} s^{-1}	Average /M^{-1} s^{-1}
MA/DMSO (λ_{exp} = 750 nm)							
20 % MA	26.5	2.93	2.94	30.0	2.46×10^{-2}	9.28×10^{-1}	**8.85×10^{-1}**
20 % MA	26.5	2.93	2.94	30.0	2.23×10^{-2}	8.41×10^{-1}	
30 % MA	26.5	2.93	2.94	30.0	1.81×10^{-2}	6.83×10^{-1}	**6.87×10^{-1}**
30 % MA	26.5	2.93	2.94	30.0	1.83×10^{-2}	6.91×10^{-1}	
40 % MA	26.5	2.93	2.94	30.0	1.42×10^{-2}	5.36×10^{-1}	**5.36×10^{-1}**
40 % MA	26.5	2.93	2.94	30.0	1.42×10^{-2}	5.36×10^{-1}	
50 % MA	22.1	2.41	2.45	25.0	1.02×10^{-2}	4.62×10^{-1}	**4.54×10^{-1}**
50 % MA	22.1	2.41	2.45	25.0	9.85×10^{-3}	4.46×10^{-1}	
60 % MA	17.7	1.93	1.96	20.0	5.72×10^{-3}	**3.23×10^{-1}**	
MMA/DMSO (λ_{exp} = 745 nm)							
10 % MMA	26.5	3.07	3.16	30.0	3.05×10^{-2}	**1.15**	
20 % MMA	26.5	3.07	3.16	30.0	2.59×10^{-2}	**9.77×10^{-1}**	
30 % MMA	26.5	3.07	3.16	30.0	1.97×10^{-2}	**7.43×10^{-1}**	
40 % MMA	26.5	3.07	3.16	30.0	1.54×10^{-2}	**5.81×10^{-1}**	
50 % MMA	22.1	2.56	2.64	25.0	1.00×10^{-2}	**4.52×10^{-1}**	
60 % MMA	17.7	2.05	2.11	20.0	6.55×10^{-3}	**3.70×10^{-1}**	
70 % MMA	13.3	1.53	1.58	15.0	3.96×10^{-3}	**2.98×10^{-1}**	
Methyl Propionate (MP)/DMSO (λ_{exp} = 745 nm)							
10 % MP	26.5	2.93	2.94	30.0	3.09×10^{-2}	**1.17**	
20 % MP	26.5	2.93	2.94	30.0	2.30×10^{-2}	**8.68×10^{-1}**	
30 % MP	26.5	2.93	2.94	30.0	1.83×10^{-2}	**6.91×10^{-1}**	
40 % MP	26.5	2.93	2.94	30.0	1.40×10^{-2}	**5.28×10^{-1}**	
50 % MP	22.1	2.41	2.45	25.0	9.30×10^{-3}	**4.21×10^{-1}**	
60 % MP	17.7	1.93	1.96	20.0	5.55×10^{-3}	**3.14×10^{-1}**	
70 % MP	13.3	1.45	1.47	15.0	3.36×10^{-3}	**2.53×10^{-1}**	

Table S3. Continued.

Solvent	$[\mathrm{I}]_0$ /mM	$[\mathrm{CuBr}]_0$ /mM	$[\mathrm{L}]_0$ /mM	$[\mathrm{TEMPO}]_0$ /mM	k_{obs} /s^{-1}	k_{act} /$\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	Average /$\mathrm{M}^{-1}\ \mathrm{s}^{-1}$
				MMA/DMF (λ_{exp} = 775 nm)			
10 % MMA	22.1	2.41	2.45	25.0	5.47×10^{-3}	$\mathbf{2.48 \times 10^{-1}}$	
20 % MMA	26.5	2.93	2.94	30.0	6.06×10^{-3}	$\mathbf{2.29 \times 10^{-1}}$	
30 % MMA	26.5	2.93	2.94	30.0	5.54×10^{-3}	$\mathbf{2.09 \times 10^{-1}}$	
40 % MMA	26.5	2.93	2.94	30.0	4.61×10^{-3}	$\mathbf{1.74 \times 10^{-1}}$	
50 % MMA	22.1	2.41	2.45	25.0	2.81×10^{-3}	$\mathbf{1.27 \times 10^{-1}}$	
60 % MMA	17.7	1.93	1.96	20.0	1.84×10^{-3}	$\mathbf{1.04 \times 10^{-1}}$	

Equilibrium Constants in Pure Solvents

The modified Fischer equation (S1) was employed for the evaluation of K_{ATRP}.[1] In this equation, I, C, and Y stand for the species indicated in Scheme S1.



Scheme S1.

$$F(\mathrm{Y}) = \left(\frac{I_0 C_0}{C_0 - I_0}\right)^2 \left(\frac{1}{C_0^{\,2}(I_0 - \mathrm{Y})} + \frac{2}{I_0 C_0 (C_0 - \mathrm{Y})} \ln\left(\frac{I_0 - \mathrm{Y}}{C_0 - \mathrm{Y}}\right) + \frac{1}{I_0^{\,2}(C_0 - \mathrm{Y})}\right) = 2k_{\mathrm{t}} K_{ATRP}^2 t + c' \qquad \text{(S1)}$$

The termination rate constants k_{t} refer to the combination reactions of the ethyl isobutyrate radicals EiB*. They are diffusion controlled and can therefore be approximated by the Smoluchowski equation:[2]

$$2k_{\mathrm{t}} = 2 \times \pi \times N_{\mathrm{A}} \times D \times \rho \qquad \text{(S2)}$$

N_{A} is Avogadro's number, D the diffusion coefficient of EiB* in the respective solvent, and ρ is the so-called reaction distance. The latter parameter can be calculated according to the method of Gorrell and Dubois (eq. S3):

$$\rho = \sqrt[3]{\frac{V_{\mathrm{m}}}{N_{\mathrm{A}}}} = \sqrt[3]{\frac{M}{dN_{\mathrm{A}}}} \qquad \text{(S3)}$$

with V_{m} and d being the molar volume and the density of the reactant, respectively. As the reactant is a radical, it must be approximated by its saturated analogue, in our case ethyl isobutyrate (EiB). With M = 116.16 g mol^{-1} and d = 0.865 g mL^{-1}, we obtain ρ = 6.06 Å.

Previously, DOSY NMR was employed to determine the diffusion coefficients D of methyl isobutyrate (MiB) in several solvents.[3] A linear correlation was observed between D and the inverse viscosities $1/\eta$, with the correlation equation (S4).

$$D \times 10^5\ [\mathrm{cm^2\ s^{-1}}] = 0.244 + 1.037/\eta\ [\mathrm{cP}] \qquad \text{(S4)}$$

In the present study, it was assumed that the difference between the diffusion coefficients of MiB and EiB are negligible. Hence, knowledge if the viscosities η of the solvents allowed the derivation of the diffusion coefficients D of EiB. Finally, with D and ρ, it was possible to calculate the rate constant k_t for the bimolecular termination reactions of EiB*.

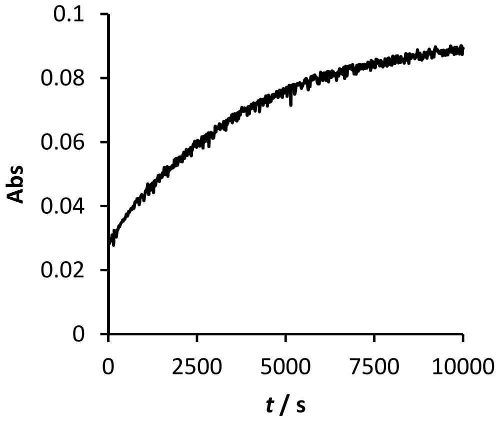
Table S4. Viscosities η of Solvents, Diffusion Coefficients D and Termination Rate Constants k_t of EiB* Radicals, and K_{ATRP} Values for the Reactions of EBiB with Cu^IBr/HMTETA at 25 °C.

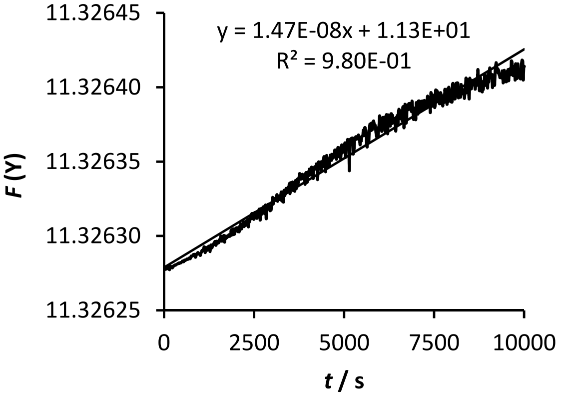
Solvent	η /cP	D /cm^2 s^{-1}	$2k_t$ /10^9 L mol^{-1} s^{-1}	K_{ATRP}
Butanone	0.43	2.66×10^{-5}	6.10	1.55×10^{-9}
Formamide	3.3	5.58×10^{-6}	1.28	2.83×10^{-6}
2,2,2-TFE	1.75	8.37×10^{-6}	1.92	7.82×10^{-9}
DMSO [a]	-	-	1.7	2.59×10^{-9}

[a] Methyl 2-bromopropionate was used as inititator, $2k_t$, referring to MBiB, was taken from ref. [3].

Recorded Absorbances and F(Y) vs. Time Plots:

Butanone (λ = 760 nm, ε = 258 L mol^{-1} cm^{-1}):
$[C]_0 = 4.88 \times 10^{-3}$ mol L^{-1}
$[EBiB]_0 = [I]_0 = 6.81 \times 10^{-2}$ mol L^{-1}



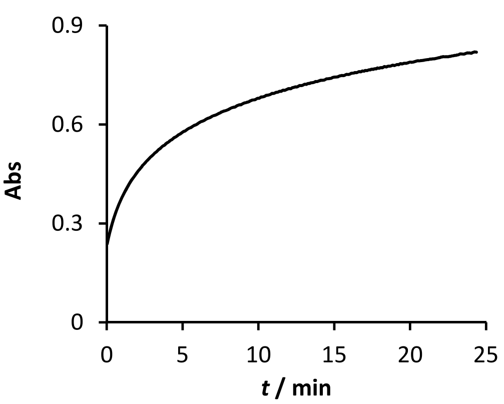


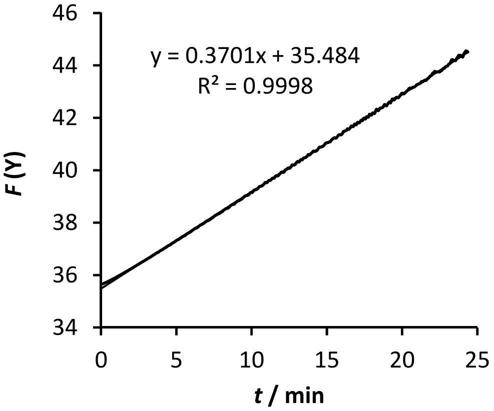
Formamide ($\lambda = 660$ nm, $\varepsilon = 253$ L mol^{-1} cm^{-1}):

(1)

$[\mathrm{C}]_0 = 5.86 \times 10^{-3}$ mol L^{-1}

$[\mathrm{EBiB}]_0 = [\mathrm{I}]_0 = 1.35 \times 10^{-2}$ mol L^{-1}



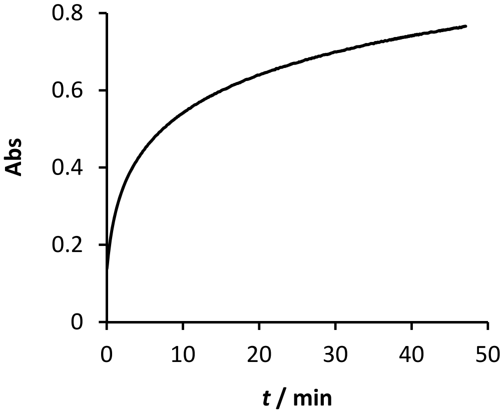


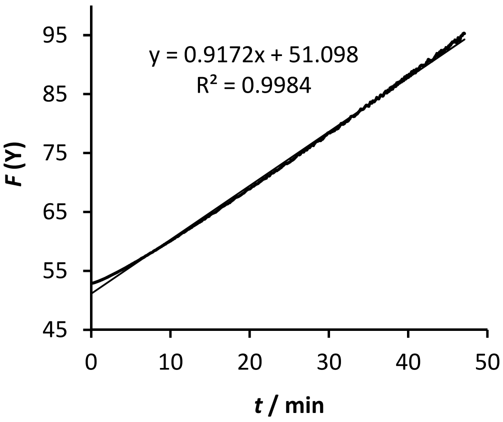
$K_{\mathrm{ATRP}} = 2.19 \times 10^{-6}$

(2)

$[\mathrm{C}]_0 = 5.86 \times 10^{-3}$ mol L^{-1}

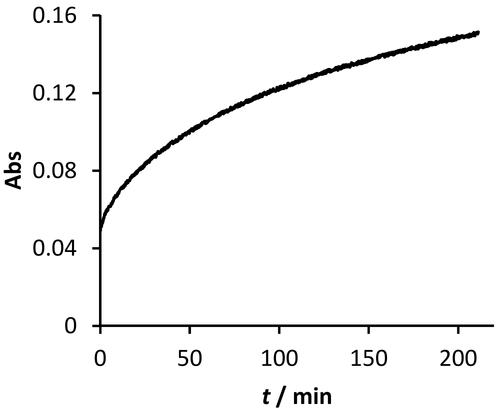
$[\mathrm{EBiB}]_0 = [\mathrm{I}]_0 = 6.77 \times 10^{-3}$ mol L^{-1}

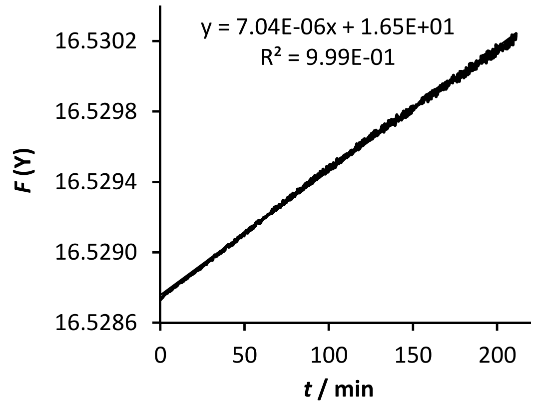




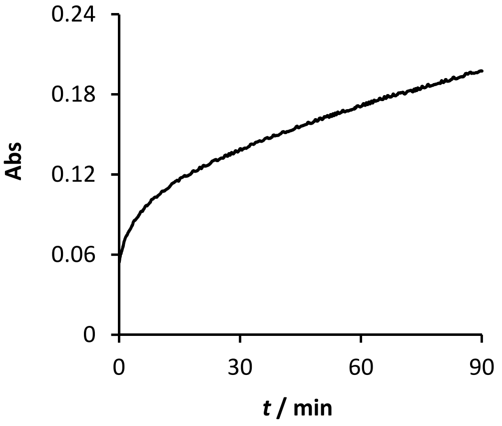
$K_{\mathrm{ATRP}} = 3.46 \times 10^{-6}$

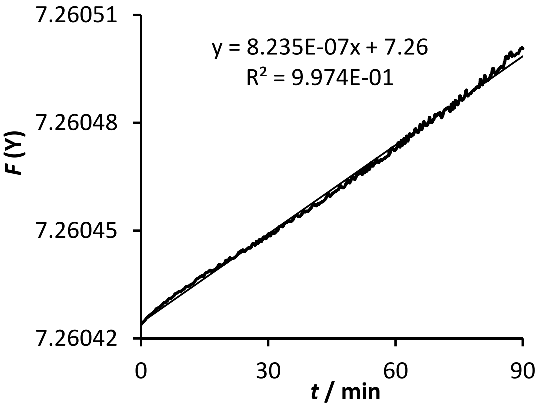
2,2,2-Trifluoroethanol (λ = 740 nm, ε = 251 L mol^{-1} cm^{-1}):
$[C]_0 = 5.86 \times 10^{-3}$ mol L^{-1}
$[EBiB]_0 = [I]_0 = 4.06 \times 10^{-2}$ mol L^{-1}





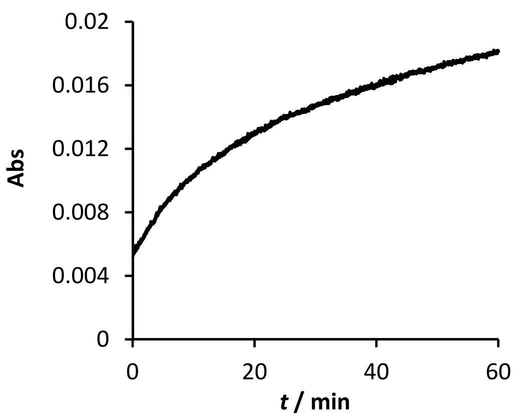
DMSO (λ = 715 nm, ε = 275 L mol^{-1} cm^{-1}):
(1)
$[C]_0 = 1.46 \times 10^{-2}$ mol L^{-1}
$[MBP]_0 = [I]_0 = 8.98 \times 10^{-2}$ mol L^{-1}

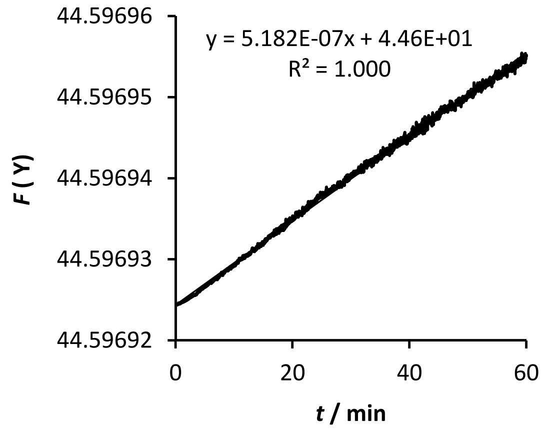




$K_{\mathrm{ATRP}} = 2.84 \times 10^{-9}$

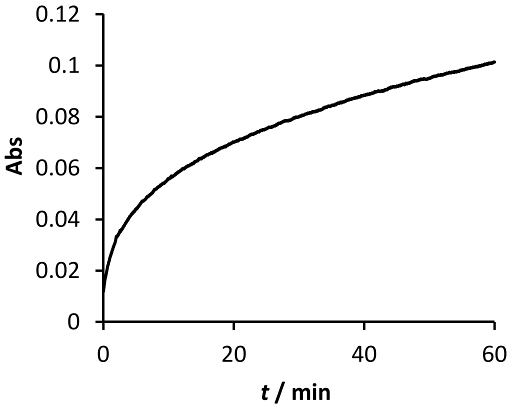
(2)
$[C]_0 = 7.32 \times 10^{-3}$ mol L^{-1}
$[MBP]_0 = [I]_0 = 7.63 \times 10^{-3}$ mol L^{-1}

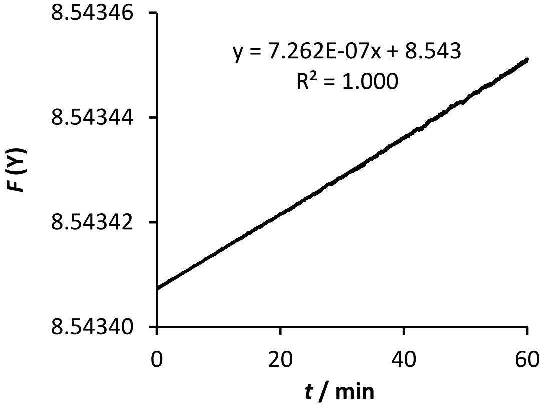




$K_{ATRP} = 2.27 \times 10^{-9}$

(3)
$[C]_0 = 7.32 \times 10^{-2}$ mol L^{-1}
$[MBP]_0 = [I]_0 = 8.80 \times 10^{-2}$ mol L^{-1}





$K_{ATRP} = 2.67 \times 10^{-9}$

Equilibrium Constants in Mixtures of MA with DMSO

Equilibrium constants K_{ATRP} were determined during polymerizations of MA in DMSO at different volume ratios V_{MA}/V_{DMSO}. The concentrations of MA have been followed by IR spectroscopy at the maximum absorbance of MA at 1658 nm.
Substitution of the time-dependent depletion of [MA], the known activator, deactivator, and initiator concentrations, as well as the propagation rate constant k_p into the following

equations yielded the equilibrium constants K_{ATRP}. A value of $k_p = 1.56 \times 10^4$ L mol^{-1} s^{-1} was employed[4] for all solvent mixtures, assuming that its dependency on the solvent is small.

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}][\mathrm{P}_n^\cdot] = k_\mathrm{p}[\mathrm{M}]K_{\mathrm{ATRP}}[\mathrm{P}_n\mathrm{Br}]\frac{[\mathrm{Cu^IL}]}{[\mathrm{BrCu^{II}L}]}$$

$$K_{\mathrm{ATRP}} = -\frac{[\mathrm{BrCu^{II}L}]}{[\mathrm{Cu^IL}][\mathrm{P}_n\mathrm{Br}]k_\mathrm{p}}\frac{\mathrm{dln[M]}}{\mathrm{d}t}$$

In a typical experiment, the absorbance of the Cu(II) species at around 770 nm slightly increased due to unavoidable termination reactions (Figure S3). In the specific case of Figure S3, one can derive that the Cu$^{\mathrm{II}}$ concentration increased by ca. 6 % in 14 h, implying that the Cu$^{\mathrm{I}}$ concentration decreased by ca. 3 %, and the chain-end functionality decreased by ca. 0.6 %. The maximum overall experimental error of K_{ATRP} arising from these concentration changes is thus 10 %.

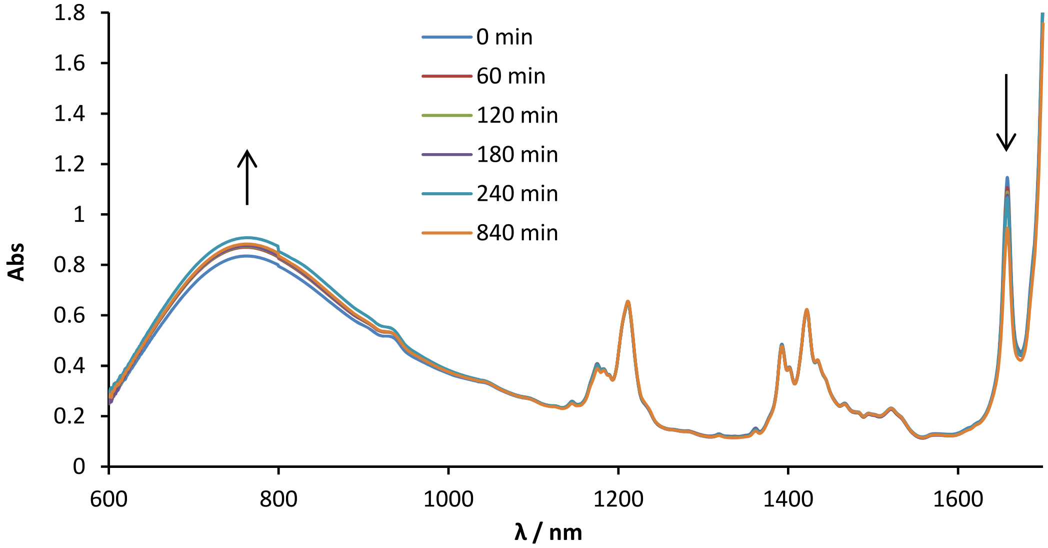


Figure S3. Evolution of the Vis-IR spectrum during the polymerization of MA in DMSO with the molar ratio of reagents: [MA]/[EBiB]/[CuBr]/[$\mathrm{BuBr_2}$]/[HMTETA] = 120/1/0.2/0.1/0.3, 70 vol-% DMSO, 25 °C; the arrows indicate the absorbance increase due to the generation of Cu(II), and the absorbance decrease due to the depletion of MA.

The left part of Figure S4 illustrates the absorbance decrease at 1658 nm due to the consumption of the monomer MA, while the right part of Figure S4 shows the corresponding logarithmic plot. The slope of its correlation straight line was used for the calculation of K_{ATRP}.

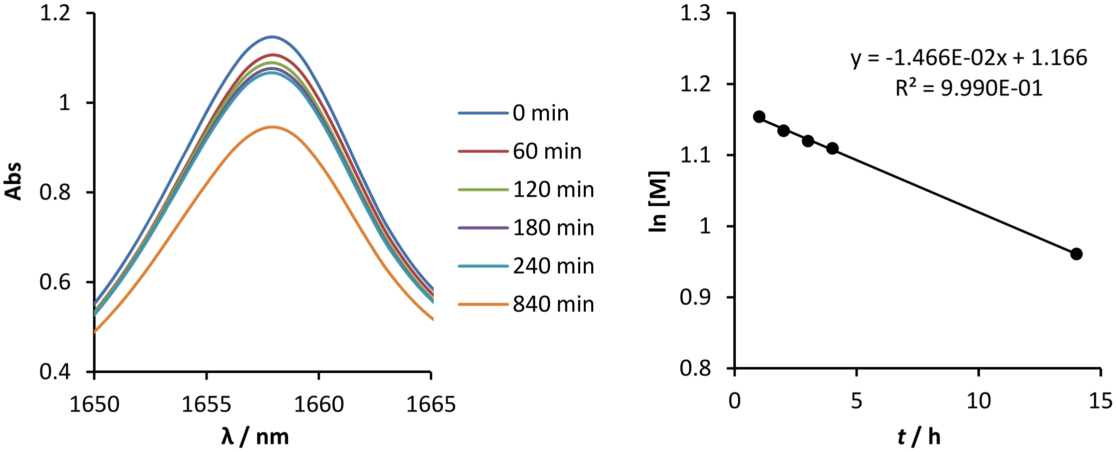


Figure S4. Evolution of the IR spectrum during the polymerization of MA in DMSO around 1658 nm (left); linear plot of ln [M] vs. time (right).

The higher the ratio V_{MA}/V_{DMSO}, the higher the absorbances around 1658 nm (Figures S5 and S6).

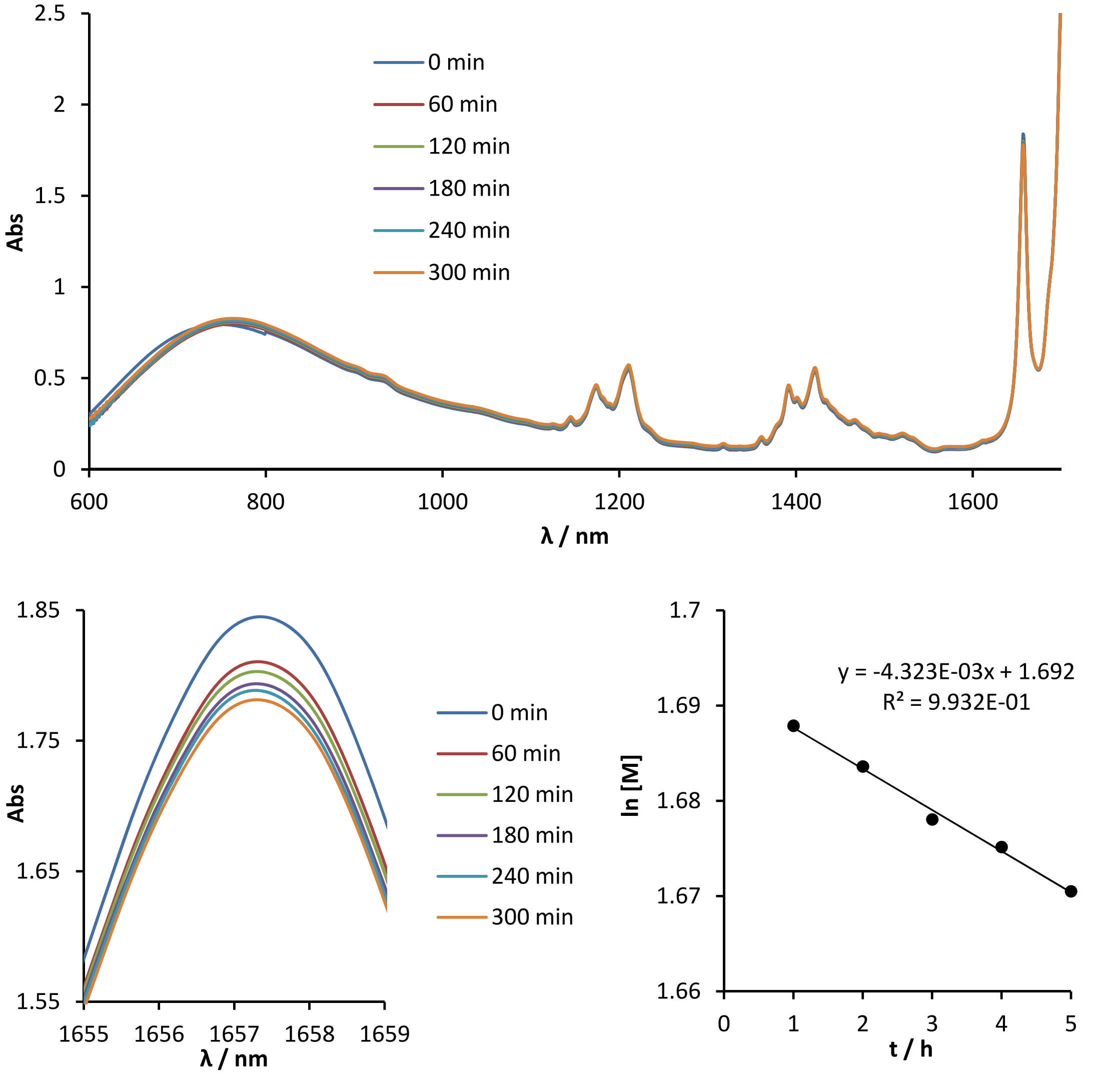


Figure S5. Top: Evolution of the Vis-IR spectrum during the polymerization of MA in DMSO with the molar ratio of reagents: [MA]/[EBiB]/[CuBr]/[$CuBr_2$]/[HMTETA] = 200/1/0.2/0.1/0.3, 50 vol-% DMSO, 25 °C. Bottom left: Zoom in at around 1658 nm. Bottom right: Linear plot of ln [M] vs. time.

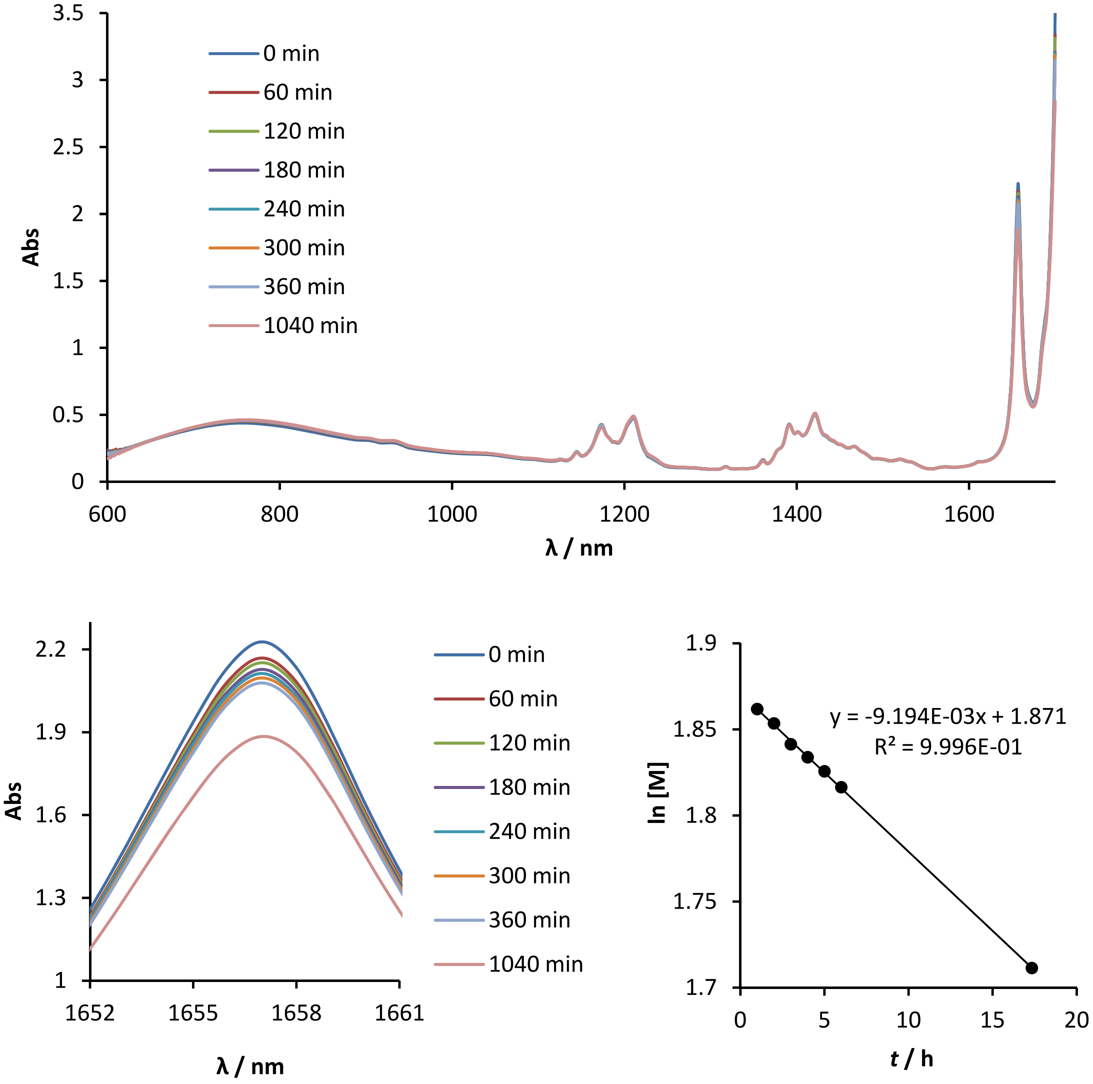


Figure S6. Top: Evolution of the Vis-IR spectrum during the polymerization of MA in DMSO with the molar ratio of reagents: [MA]/[EBiB]/[CuBr]/[$CuBr_2$]/[HMTETA] = 240/1/0.2/0.05/0.25, 40 vol-% DMSO, 25 °C. Bottom left: Zoom in at around 1658 nm. Bottom right: Linear plot of ln [M] vs. time.

Spectrophotometric Titrations

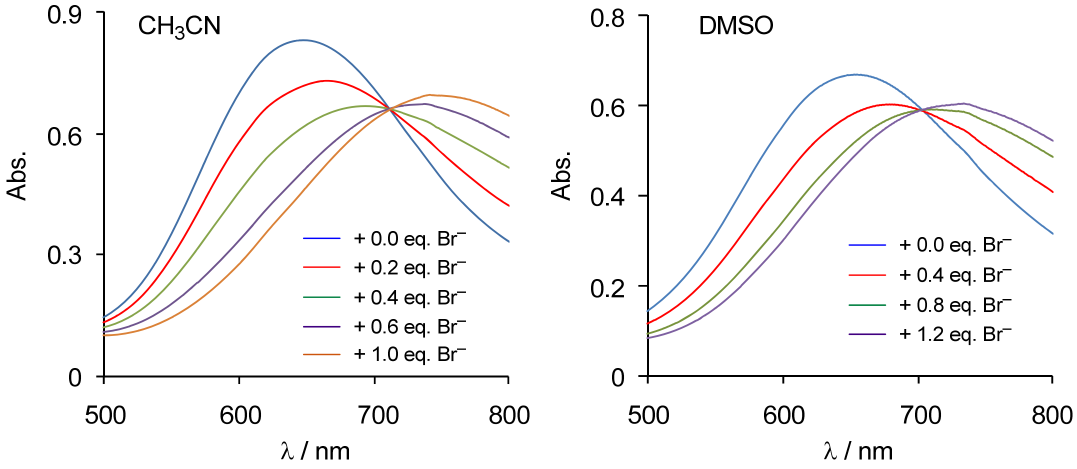


Figure S7. Bathochromic shifts of the absorbance maxima during the titration of 2.27 mM $Cu^{II}(TfO)_2$/HMTETA in CH_3CN (left), and 2.76 mM $Cu^{II}(TfO)_2$/HMTETA in DMSO (right) with tetrabutylammonium bromide, 25 °C.

Solvatochromic Parameters

Table S5. Kamlet-Taft Parameters[a] and Hildebrand Solubility Parameters[b] of the Solvents.

Solvent	π^*	α	β	δ	$(\delta_H)^2$ /cal$^{1/2}$ cm$^{-3/2}$
Anisole	0.73	0	0.22	1	97.6
Acetonitrile	0.75	0.19	0.40	0	161.3
Acetone	0.71	0.08	0.48	0	210.3
Butanone	0.67	0.06	0.48	0	132.3
DMSO	1.00	1.00	0	0	144.0
DMF	0.88	0	0.69	0	127.7
Dimethylacetamide	0.88	0	0.76	0	146.4
Formamide	0.97	0.71	0.60	0	176.9
N-Methylpyrrolidone	0.92	0	0.77	0	139.2
Propylene carbonate	0.83	0	0.4	0	98.0
MeOH	0.60	0.93	0.66	0	86.5
EtOH	0.54	0.83	0.75	0	136.9
2-PrOH	0.48	0.76	0.95	0	368.6
2,2,2-TFE	0.73	1.51	0	0	116.6

[a] From refs. [5]; [b] from refs. [6].

Quantum Chemical Calculations

Unrestricted B3LYP was employed for the open-shell systems [Br–Cu^{II}/HMTETA]$^{+}$ and EiB*. Figure S8 depicts all optimized gas phase structures. For the modeling of solvation by DMSO and acetone, the PCM with UFF radii was used.

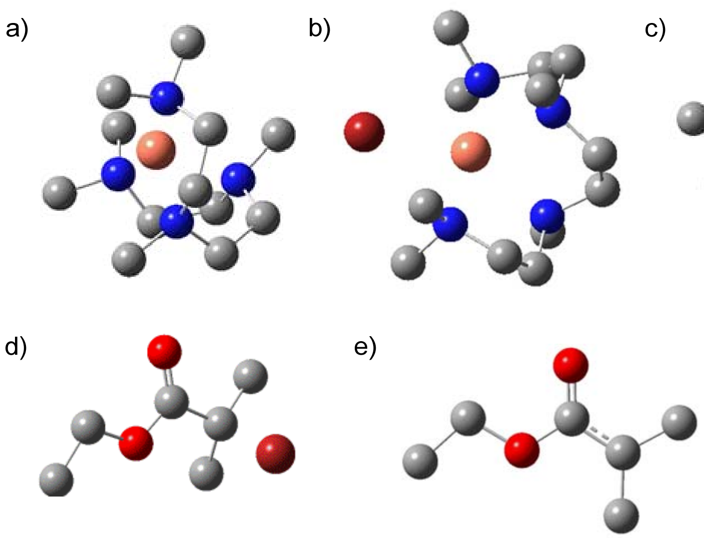


Figure S8. Optimized gas phase structures of a) [Cu^{I}/HMTETA]$^{+}$, b) [Br–Cu^{II}/HMTETA]$^{+}$ (trigonal bipyramid), c) [Br–Cu^{II}/HMTETA]$^{+}$ (square pyramid), d) EBiB, e) EiB*. The H-atoms have been omitted for the sake of clarity.

Table S6. MP2 Total Energies (at 0 K) of Cu-Complexes and Thermal Corrections to ΔG_{298} on the B3LYP level (in Hartrees).

	[Cu^{I}/HMTETA]$^{+}$	[Br–Cu^{II}/HMTETA]$^{+}$ (trigonal bipyramid)	[Br–Cu^{II}/HMTETA]$^{+}$ (square pyramid)
MP2-Energy in Acetone	-2331.180261	-4903.690472	-4903.694837
MP2-Energy in DMSO	-2331.181815	-4903.692766	-4903.697181
Thermal Correction to 298 K	0.389426	0.389475	0.387608

Table S7. MP2 Total Energies (at 0 K) of EBiB and EiB* and Thermal Corrections to ΔG_{298} on the B3LYP level (in Hartrees).

	EBiB	EiB*
MP2-Energy in Acetone	-2957.00023	-384.4363492
MP2-Energy in DMSO	-2957.000531	-384.4366635
Thermal Correction to 298 K	0.127381	0.124622

Chemicals

All reagents employed in this study, CuBr (99.999%, Aldrich), $CuBr_2$ (99.999%, Aldrich), $Cu(CH_3CN)_4BF_4$ (97%, Aldrich), ethyl α-bromoisobutyrate (EBiB, 99%, Aldrich), methyl α-bromoisobutyrate (MBriB, 99%, Aldrich), methyl α-bromopropionate (MBP, 98% Aldrich), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich), 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO, 99%, Aldrich), and tetrabutylammonium bromide (>99.0%, Aldrich) were obtained from commercial sources and used without further purification. All solvents were obtained from commercial sources and dried prior to use, either by molecular sieves, refluxing over Mg, or by columns filled with alumina. Monomers methyl acrylate (MA, 99 %, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were filtered through basic alumina in order to remove inhibitors. All liquids (initiators, ligand, monomers, solvents) were deoxygenated by purging with nitrogen.

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