Supporting Information for

Use of spin traps to measure the addition and fragmentation rate coefficients of small molecule RAFT-adduct radicals

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Experimental Procedures

RAFT agent - \textit{tert}-butyl dithiobenzoate, TB, was synthesized and characterized as described before\textsuperscript{1}. \textit{2-Methyl-2-nitrosopropane} (MNP) was used as received. All the reaction mixtures were prepared in the dark by dissolving of given amounts of MNP and a RAFT agent in benzene, solutions were poured in the ampule with inner diameter 2.2 mm, degassed and sealed. The ESR spectra were detected at room temperature by ESR spectroscopy using a RE-1307 instrument, equipped with a universal X-band (9.4 GHz) cavity using 100 kHz field modulation, 30 mW microwave power and amplitude in field modulation 0.03 G. Data processing was carried out using the EPR (v. 2.3) software package. The amount of paramagnetic centers was determined by comparison of the integral of the ESR signal of the sample with that of a carbon black standard of known spin number.

\textsuperscript{1} Chernikova E., Morozov A., Leonova E., Garina E., Golubev V., Bui C., Charleux B., \textit{Macromolecules}. 2004, \textbf{37}, 6329
Fig. S1. ESR-spectrum of DTBN adduct ($A_\text{N}=14.50\pm0.05$ G) observed on irradiation by visible light of the system MNP–benzene at 20°C.

Fig. S2. ESR-spectrum of intermediate radical observed on heating the system TB–AIBN–styrene ($A_{\text{OH}} = 3.65$ G, $A_{\text{mH}} = 1.34$ G, $A_{\text{pH}} = 3.99$ G, $A_{\text{BH}} = 0.42$ G) at 90°C.
Fig. S3. Kinetic curves of accumulation and consumption of intermediate radical Int (1) and DTBN (2) in the system TB–MNP–benzene after switch-off of MNP photolysis: [TB] \times 10^2 = 1 \text{ (a)}, 3 \text{ (b), 9 (c), [MNP] = 10^{-2} mol/L at 20^\circ C.}

![Kinetic curves of accumulation and consumption of intermediate radical Int (1) and DTBN (2)](image)

Table S1. Values of addition rate coefficients determined under various TB concentrations.

<table>
<thead>
<tr>
<th>[TB] \times 10^2, mol/L</th>
<th>[MNP] \times 10^2, mol/L</th>
<th>k_{ad} \times 10^6, L mol^{-1} s^{-1}</th>
<th>average k_{ad}, L mol^{-1} s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

(5\pm1) \times 10^6
Computational Procedures

Standard ab initio molecular orbital theory and density functional theory calculations were performed using Gaussian 03\textsuperscript{2} and Molpro 2006.1\textsuperscript{3} software, using a high-level of theory, previously shown to reproduce experimental equilibrium constants for addition-fragmentation in RAFT polymerization to within chemical accuracy.\textsuperscript{4} Geometries of all species were optimised at the B3-LYP/6-31G(d) level of theory and scaled frequency calculations were also performed at that level; this level has been previously shown to reproduce geometries and frequencies obtained via high-level ab initio methods.\textsuperscript{5} Conformations of all species were systematically screened at the B3-LYP/6-31G(d) level of theory. Improved energies were then obtained using our W1-ONIOM method, as defined and evaluated in our previous papers.\textsuperscript{6} In the present work the system was sufficiently small to allow for a two-layer approach where the reaction of •CH\textsubscript{3} with S=C(H)SCH\textsubscript{3} was treated at W1\textsuperscript{7}; the substituent effects of the remaining system were treated at the G3(MP2)-RAD\textsuperscript{8} level. Partition functions and associated thermodynamic quantities (at 293.15 K) were calculated using the standard textbook formulae for an ideal gas under the rigid-rotor/harmonic oscillator approximation. These harmonic oscillator values were then corrected by treating all low frequency torsional modes as hindered internal rotations using the torsional eigenvalue summation (TES) method, applied to rotational potentials calculated from relaxed B3-LYP/6-31G(d) scans at 60° resolution. Full details of this method are provided in a recent publication.\textsuperscript{9} The gas-phase calculations were corrected for solvent effects in benzene, using a thermodynamic cycle in which the solvation energies were modelled using the PCM-UAHF method\textsuperscript{10} at the HF/6-31G(d) level of theory. All solvation energy

---


calculations were performed using the SCFVAC keyword in Gaussian so that the solvation energy instead of the total free energy in the solvent, could be extracted and combined with higher-level calculations of the free energy in gas phase so as to calculate the solution phase free energy of reaction, $\Delta G(\text{soln})$ via equation 1.

$$
\Delta G(\text{soln}) = \Delta G(\text{g}) + \Delta G(\text{solv}) + \Delta nRT \ln(\text{RT}/P^\circ) \quad (1)
$$

This equation includes the correction term $\Delta nRT \ln(\text{RT}/P^\circ)$, where $P^\circ$ is the standard pressure in the gas-phase calculations, $\Delta n$ is the change in the number of moles of solvated species on reaction and is equal to one in this case. This term is needed to account for the passage from 1 atm (g) to 1 mol/L (soln). The equilibrium constant $K$ of the reaction was then calculated using the equation 2.

$$
K(T) = (c^\circ)^{\Delta n}\exp(-\Delta G(\text{soln})/RT) \quad (2)
$$

where $c^\circ$ is the standard unit of concentration and is equal to 1 mol/L in solution.
Table S2 Total Energies, Entropies, Thermal Corrections and Solvation Energies (units are Hartrees unless otherwise noted).

<table>
<thead>
<tr>
<th>mol</th>
<th>Entropy at 293K (J/mol K)</th>
<th>Thermal correction at 293 K</th>
<th>Zero point vibrational energy</th>
<th>High level correction</th>
<th>B3LYP/6-31G*</th>
<th>ROMP2/6-31G*</th>
<th>ROMP2/GTMP2Large</th>
<th>B3LYP/6-31G*</th>
<th>UCCSD(T)/6-31G*</th>
<th>MP2/6-31G*</th>
<th>G3(MP2)‐RAD E (no ZPVE)</th>
<th>W1 E (no ZPVE)</th>
<th>ONIOM E (no ZPVE)</th>
<th>ORCCSD(T)/6-31G*</th>
<th>COSMORS in benzene at 293.15 K</th>
<th>UAHF-PCM in benzene at 293.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu‐SC(Ph)StBu</td>
<td>628.63830</td>
<td>0.02125</td>
<td>0.33736</td>
<td>-0.44638</td>
<td>-1381.80467</td>
<td>-1378.60278</td>
<td>-1379.48566</td>
<td>-0.44638</td>
<td>-1381.80467</td>
<td>-1378.60278</td>
<td>-1379.48566</td>
<td>-0.44638</td>
<td>-1382.02889</td>
<td>-1382.74047</td>
<td>-10.45</td>
<td>-2.26</td>
</tr>
<tr>
<td>S=C(Ph)StBu</td>
<td>489.96990</td>
<td>0.01467</td>
<td>0.21799</td>
<td>-0.32946</td>
<td>-1223.98214</td>
<td>-1221.38650</td>
<td>-1222.04634</td>
<td>-0.32946</td>
<td>-1223.98214</td>
<td>-1221.38650</td>
<td>-1222.04634</td>
<td>-0.32946</td>
<td>-1221.55881</td>
<td>-1222.54810</td>
<td>-8.16</td>
<td>-0.20</td>
</tr>
<tr>
<td>r.tBu</td>
<td>326.61070</td>
<td>0.00715</td>
<td>0.11499</td>
<td>-0.11693</td>
<td>-157.79832</td>
<td>-157.17694</td>
<td>-157.39216</td>
<td>-0.11693</td>
<td>-157.79832</td>
<td>-157.17694</td>
<td>-157.39216</td>
<td>-0.11693</td>
<td>-157.58084</td>
<td>-157.58084</td>
<td>-2.27</td>
<td>-0.15</td>
</tr>
<tr>
<td>tBu-SC(Ph)SMe</td>
<td>-</td>
<td>-</td>
<td>-0.36166</td>
<td>-1263.86535</td>
<td>-1261.90811</td>
<td>-1261.82407</td>
<td>-1262.38245</td>
<td>-0.36166</td>
<td>-1263.86535</td>
<td>-1261.90811</td>
<td>-1261.82407</td>
<td>-0.36166</td>
<td>-1261.09811</td>
<td>-1261.10981</td>
<td>-2.27</td>
<td>-0.15</td>
</tr>
<tr>
<td>S=C(Ph)SMe</td>
<td>-</td>
<td>-</td>
<td>-0.24474</td>
<td>-1106.04526</td>
<td>-1103.88538</td>
<td>-1104.38813</td>
<td>-1104.75879</td>
<td>-0.24474</td>
<td>-1106.04526</td>
<td>-1103.88538</td>
<td>-1104.38813</td>
<td>-0.24474</td>
<td>-1104.01131</td>
<td>-1104.58679</td>
<td>-8.16</td>
<td>-0.20</td>
</tr>
<tr>
<td>r.tBu</td>
<td>-</td>
<td>-</td>
<td>-0.11693</td>
<td>-157.79832</td>
<td>-157.17694</td>
<td>-157.39216</td>
<td>-157.58084</td>
<td>-0.11693</td>
<td>-157.79832</td>
<td>-157.17694</td>
<td>-157.39216</td>
<td>-0.11693</td>
<td>-157.58084</td>
<td>-157.58084</td>
<td>-2.27</td>
<td>-0.15</td>
</tr>
<tr>
<td>Me-SC(H)SMe</td>
<td>-</td>
<td>-</td>
<td>-0.14512</td>
<td>-914.86617</td>
<td>-913.37196</td>
<td>-913.60526</td>
<td>-913.83768</td>
<td>-0.14512</td>
<td>-914.86617</td>
<td>-913.37196</td>
<td>-913.60526</td>
<td>-0.14512</td>
<td>-913.35926</td>
<td>-913.83768</td>
<td>-8.16</td>
<td>-0.20</td>
</tr>
<tr>
<td>S=C(H)SMe</td>
<td>-</td>
<td>-</td>
<td>-0.11292</td>
<td>-875.08805</td>
<td>-873.56611</td>
<td>-873.83292</td>
<td>-873.63116</td>
<td>-0.11292</td>
<td>-875.08805</td>
<td>-873.56611</td>
<td>-873.83292</td>
<td>-0.11292</td>
<td>-874.01089</td>
<td>-876.93905</td>
<td>-8.16</td>
<td>-0.20</td>
</tr>
</tbody>
</table>
Table S3. Rotational potentials (B3LYP/6-31G(d)), entropy (S) and thermal correction (TC) from hindered rotor and harmonic oscillator of individual functional groups and estimated low-mode vibrational frequencies for corresponding rotations used for calculation of the propagation rate coefficients.

M e t h y l

\[
\begin{array}{l}
\text{Methyl rotation} \\
\text{Estfreq = 127.3437 cm}^{-1} \\
\text{S HO = 12.3442 J/mol K} \\
\text{S HR = 13.6382 J/mol K} \\
\text{TC HO = 1.7552 kJ/mol} \\
\text{TC HR = 1.7540 kJ/mol}
\end{array}
\]

\[
\begin{array}{l}
\text{t B u}
\end{array}
\]
S=C(Ph)-StBu

<table>
<thead>
<tr>
<th>S-C(Ph) rotation</th>
<th>S-tBu rotation</th>
<th>C-Ph rotation</th>
<th>Methyl rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estfreq = 43.9270 cm⁻¹</td>
<td>Estfreq = 61.2654 cm⁻¹</td>
<td>Estfreq = 32.9093 cm⁻¹</td>
<td>Estfreq = 265.0848 cm⁻¹</td>
</tr>
<tr>
<td>TC HO = 2.1843 kJ/mol</td>
<td>TC HO = 2.0789 kJ/mol</td>
<td>TC HO = 2.2460 kJ/mol</td>
<td>TC HO = 1.1873 kJ/mol</td>
</tr>
<tr>
<td>TC HR = 2.2354 kJ/mol</td>
<td>TC HR = 2.2570 kJ/mol</td>
<td>TC HR = 2.4572 kJ/mol</td>
<td>TC HR = 1.3961 kJ/mol</td>
</tr>
</tbody>
</table>

Graphs showing dihedral angles for S-C(Ph), S-tBu, C-Ph, and Methyl rotations.
<table>
<thead>
<tr>
<th>S-C(Ph) rotation</th>
<th>S-tBu rotation</th>
<th>C-Ph rotation</th>
<th>Methyl rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estfreq = 40.2998 cm⁻¹</td>
<td>Estfreq = 61.2654 cm⁻¹</td>
<td>Estfreq = 49.2041 cm⁻¹</td>
<td>Estfreq = 305.4744 cm⁻¹</td>
</tr>
<tr>
<td>TC HO = 2.2045 kJ/mol</td>
<td>TC HO = 2.0896 kJ/mol</td>
<td>TC HO = 2.1552 kJ/mol</td>
<td>TC HO = 1.0516 kJ/mol</td>
</tr>
<tr>
<td>TC HR = 2.3185 kJ/mol</td>
<td>TC HR = 2.2101 kJ/mol</td>
<td>TC HR = 2.2552 kJ/mol</td>
<td>TC HR = 1.2077 kJ/mol</td>
</tr>
</tbody>
</table>
Appendix S1. B3-LYP/6-31G(d) Optimized Geometries

**tBuS-C(Ph)StBu**

<table>
<thead>
<tr>
<th>Method</th>
<th>Parameters</th>
<th>E (kJ/mol)</th>
<th>δH (kJ/mol)</th>
<th>δS (J/K/mol)</th>
<th>RMSD (Å)</th>
<th>RMSF (Å)</th>
<th>Thermal (K)</th>
<th>Dipole (D)</th>
<th>PG</th>
<th>X(C15H23S2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G*</td>
<td>Opt freq=noraman</td>
<td>-1381.806</td>
<td>-1581.619</td>
<td>0.77225</td>
<td>7.139e-09</td>
<td>1.329e-06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>maxdisk=402653184</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>B3LYP/6-31G</td>
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<td>-1223.982</td>
<td>-1423.795</td>
<td>0.56403</td>
<td>4.672e-09</td>
<td>1.48e-05</td>
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<td></td>
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<td></td>
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</tr>
</tbody>
</table>

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**1.1**

```
\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Method & Parameters & E (kJ/mol) & δH (kJ/mol) & δS (J/K/mol) & RMSD (Å) & RMSF (Å) \\
\hline
B3LYP/6-31G* & Opt freq=noraman & -1381.806 & -1581.619 & 0.77225 & 7.139e-09 & 1.329e-06 \\
 & maxdisk=402653184 & & & & & \\
B3LYP/6-31G & Optim freq=noraman maxdisk=402653184 & -1223.982 & -1423.795 & 0.56403 & 4.672e-09 & 1.48e-05 \\
 & maxdisk=402653184 & & & & & \\
\hline
\end{tabular}
\end{table}
```
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CH3.freq\0,2,S,-0.6882309216,1.625949055,-0.2302971907\C,-0.6047201199,1.5711078656,1.6029992764\H,0.4361942341,1.5969963754,1.9361945197\H ,-1.1024599709,0.6844325708,2.000367826\H,-1.126003578,2.4657472605,1.9552062312\C,0.2456888881,0.2399582127,-0.7175947999,0.6910030919,0.3169943529,-1.70742147\S,-0.0347888506,-1.3639906191,-0.0635584324\C,1.5405031227,-2.1760497057,-0.5050915666,1.4568897965,-3.2240894674,-0.2055881155\H,2.3813213504,-1.7129462715,0.0250580372,1.715615695,-2.1287300303,-1.5848908976\Version=IA64L-G03RevC.02\State=2-A\HF=-914.8661692\S2=0.755421\S2-1=0.\S2A=0.750021\RMSD=4.482e-09\RMSF=8.561e-06\Dipole=0.5848833,-0.3016247,0.2564161\FG=C01 \[X(C3H7S2)\] @
S=C(H)SMe

1\1\GINC-AC18\POpt\RB3LYP\Gen\C2H4S2\CYL509\07-Jan-2008\0\#B3LYP/GEN OPT FREQ=NORAMAN MAXDISK=1342177280\SCHSCH3.1.freq\0,1,S,0.158221240 3,0,-1.055574083\C,0.0121496708,0.,0.664183356\S,-1.3937103601,0.,1.4 767510964\H,0.970997075,0.,1.1823430971\C,1.962836935,0.,-1.298169525 \H,2.4112707329,-0.8940256164,-0.8716931472\H,2.4112707329,0.894025616 4,-0.8716931472\H,2.1243677418,0.,-2.3738694386\Version=IA64L-G03RevC .02\State=1-A\HF=-875.0880467\RMSD=4.455e-09\RMSF=3.095e-05\Dipole=1. 4091687,0.,-0.6606179\PG=CS \[SG(C2H2S2),X(H2)\] @

r.Me

1\1\GINC-AC28\POpt\UB3LYP\Gen\C1H3(2)\CYL509\20-Feb-2008\0\#B3LYP/GEN 6D INT\GRID=ULTRAFINE\ OPT FREQ=NORAMAN MAXDISK=1342177280\CH3.freq\0,2\H,-0.1617164304,-0.3245651343,-1.0209889129\C,0.0002146569,0.0003 717968,-0.0001517853\H,0.8958563892,-0.302331803,0.5291021344\H,0.73 54279002,0.6246675337,0.4927974904\Version=IA64L-G03RevC.02\State=2-A 1\HF=-39.8426447\S2=0.753502\S2-1=0.\S2A=0.750006\RMSD=5.766e-09\RMSF= 2.535e-05\Dipole=-0.0006374,-0.0011039,0.0004507\FG=C03V \[C3(C1),3SGV( H1)\] @
Appendix S2. CALCULATION OF TERMINATION RATE COEFFICIENT

\[
\frac{d[DTBN]}{dt} = k_{rT}[MNP][r]
\]

\[
\frac{d[Int]}{dt} = k_{ad}[TB][r] - k_{nT}[Int] - k_{rT}''[Int]^2
\]

\[
\frac{d[r]}{dt} = -k_{rT}[MNP][r] - k_{ad}[TB][r] + k_{nT}[Int] = 0
\]

\[
[r] = \frac{k_{nT}[Int]}{k_{rT}[MNP] + k_{ad}[TB]}
\]

\[
\frac{d[DTBN]}{dt} = \frac{k_{rT}[MNP][r]}{k_{rT}[MNP] + k_{ad}[TB]}
\]

\[
\frac{d[Int]}{dt} = \frac{k_{nT}[TB][r] - k_{nT}[Int] - k_{rT}''[Int]^2}{k_{rT}[MNP] + k_{ad}[TB]} = \frac{k_{nT}[TB]k_{nT}[Int]}{k_{rT}[MNP] + k_{ad}[TB]}
\]

\[
\frac{d[r]}{dt} = -k_{nT}[Int]k_{rT}[MNP] - k_{rT}''[Int]^2 (k_{rT}[MNP] + k_{ad}[TB])
\]

\[
\frac{d[DTBN]}{dt} - \frac{d[DTBN]}{dt} = -k_{nT}[Int]k_{rT}[MNP] - k_{rT}''[Int]^2 (k_{rT}[MNP] + k_{ad}[TB]) = -k_{nT}[Int](k_{rT}[MNP] + k_{ad}[TB])
\]

\[
k_{nT}k_{rT}[MNP] \left( \frac{d[Int]}{dt} \frac{k_{rT}[MNP]}{d[DTBN]} + 1 \right) = -k_{rT}''[Int](k_{rT}[MNP] + k_{ad}[TB])
\]

\[
k_{rT}'' = \frac{-\left( \frac{d[Int]}{dt} \frac{k_{rT}[MNP]}{d[DTBN]} + 1 \right)k_{nT}k_{rT}[MNP]}{[Int](k_{rT}[MNP] + k_{ad}[TB])}
\]