UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Quantitative first principles based kinetic modeling for the synthesis of well-defined macromolecular architectures

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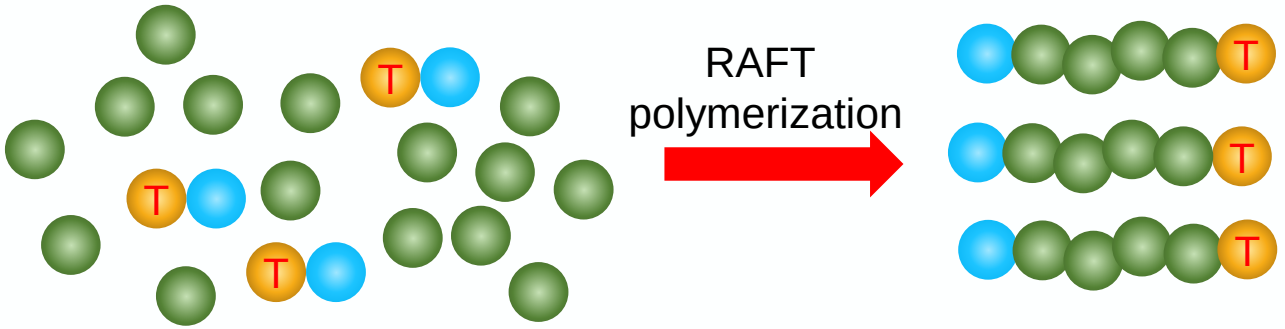
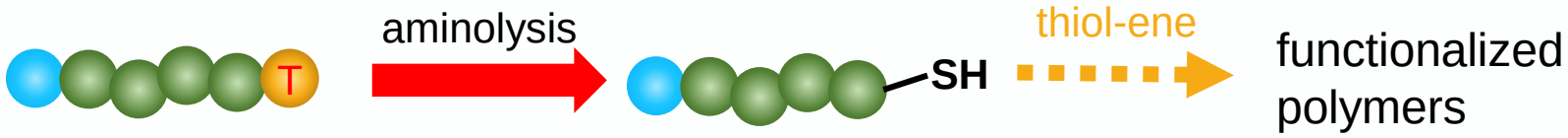
Contents: 2 case studies related to Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization

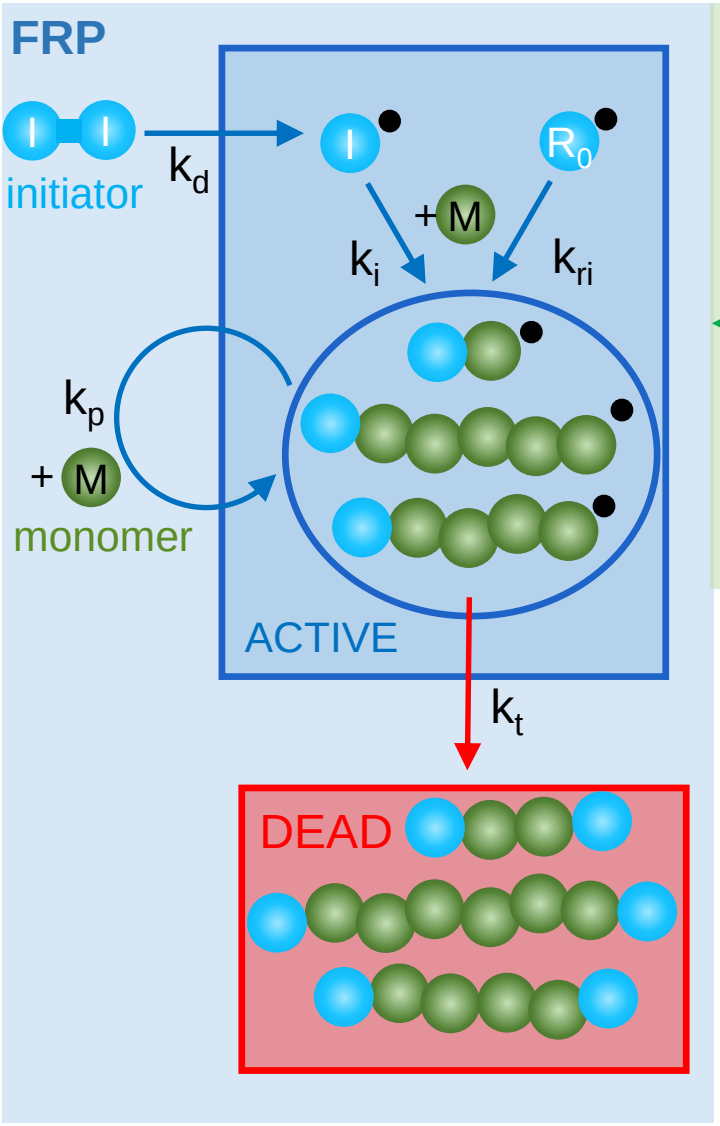
1. RAFT polymerization of styrene ( ) using a trithiocarbonate ( )
   - Calculation of **addition-fragmentation** rate coefficients
   - Application in a **microkinetic model**

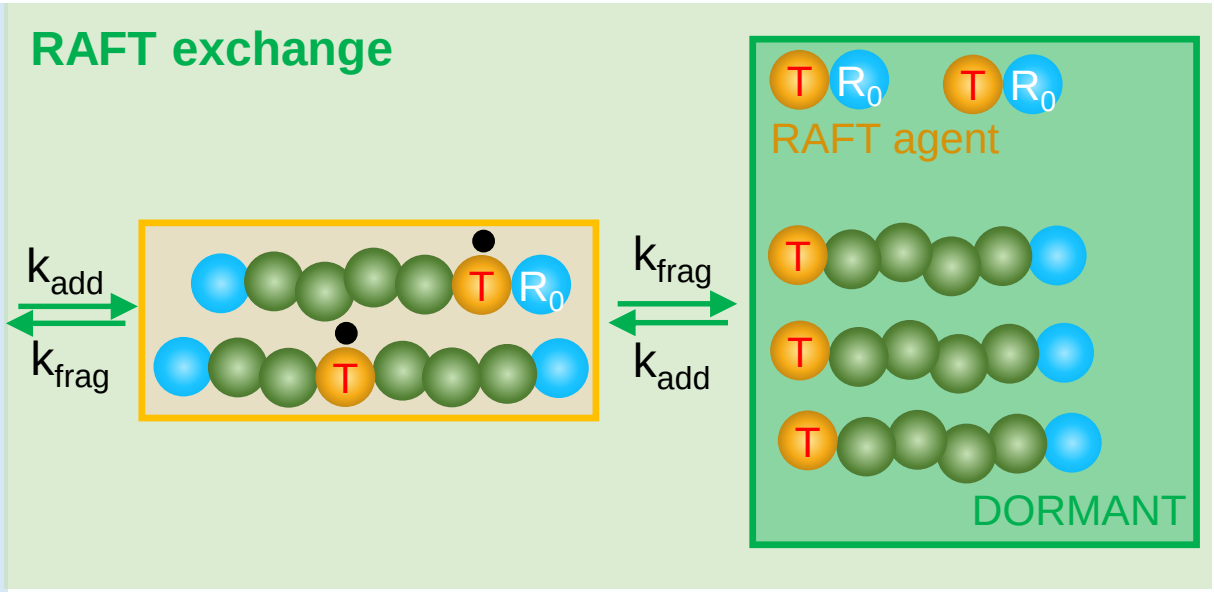


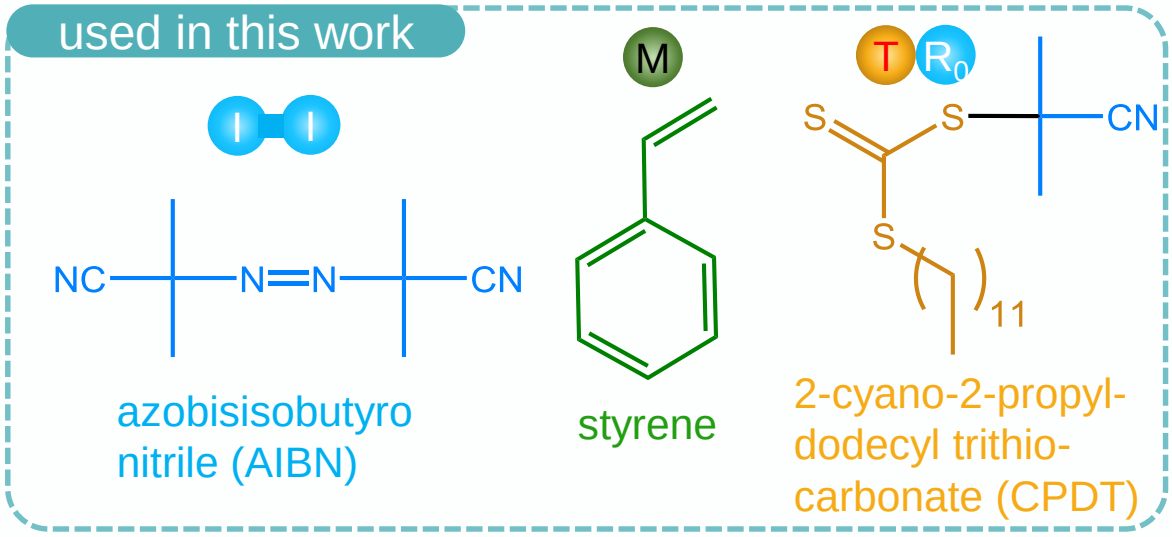
2. The **aminolysis of RAFT-macromolecules**
   - Determination of the reaction mechanism
   - calculation of **rate coefficients** for a variety of RAFT-agents



How do RAFT agents help us to obtain control over the chain length in radical polymerization

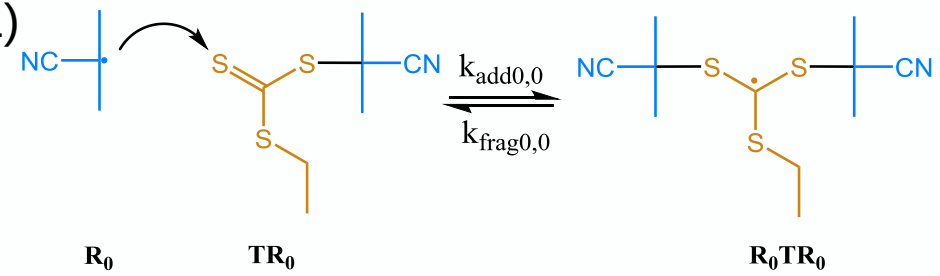






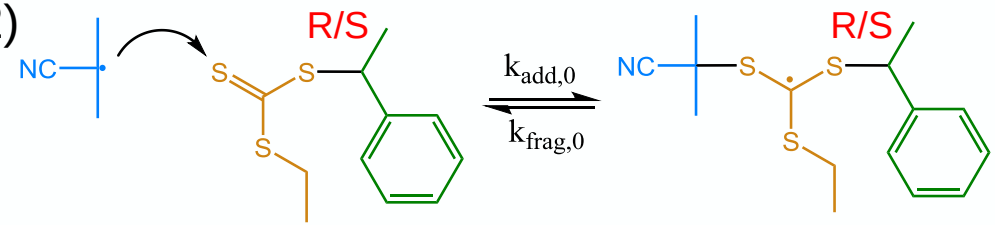
Ab initio calculation of addition-fragmentation reactions using a dimer model: 4 model reactions

1)



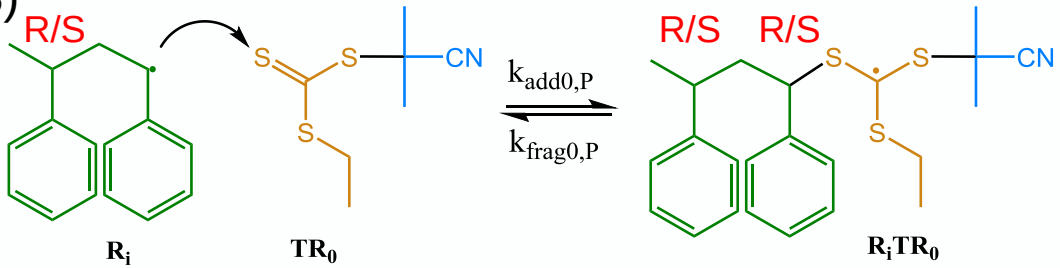
R_0 TR_0 R_0TR_0

2)



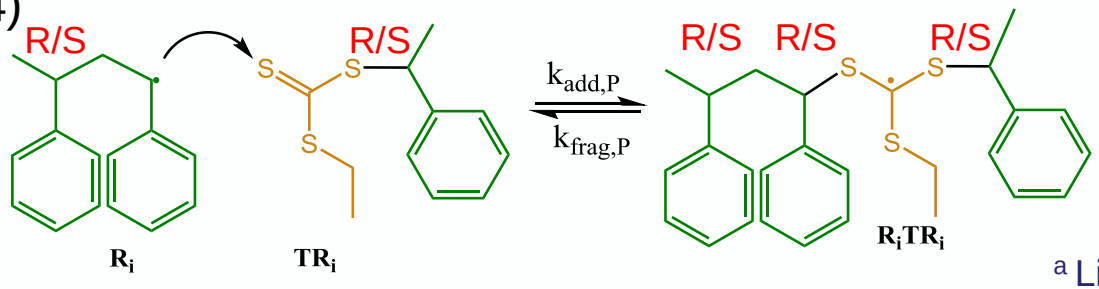
R_0 TR_i R_0TR_i

3)



R_i TR_0 R_iTR_0

4)



R_i TR_i R_iTR_i

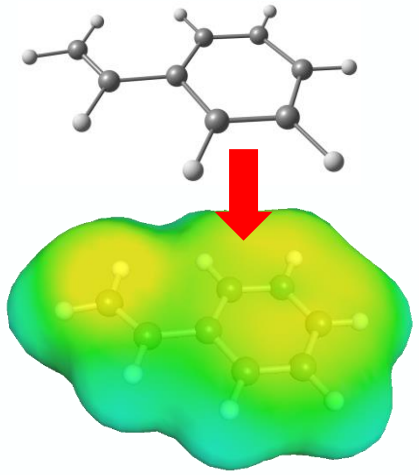
Model assumptions

- dimer radical to model macroradical[a]
- ethyl group to model dodecyl group

Ab initio calculation

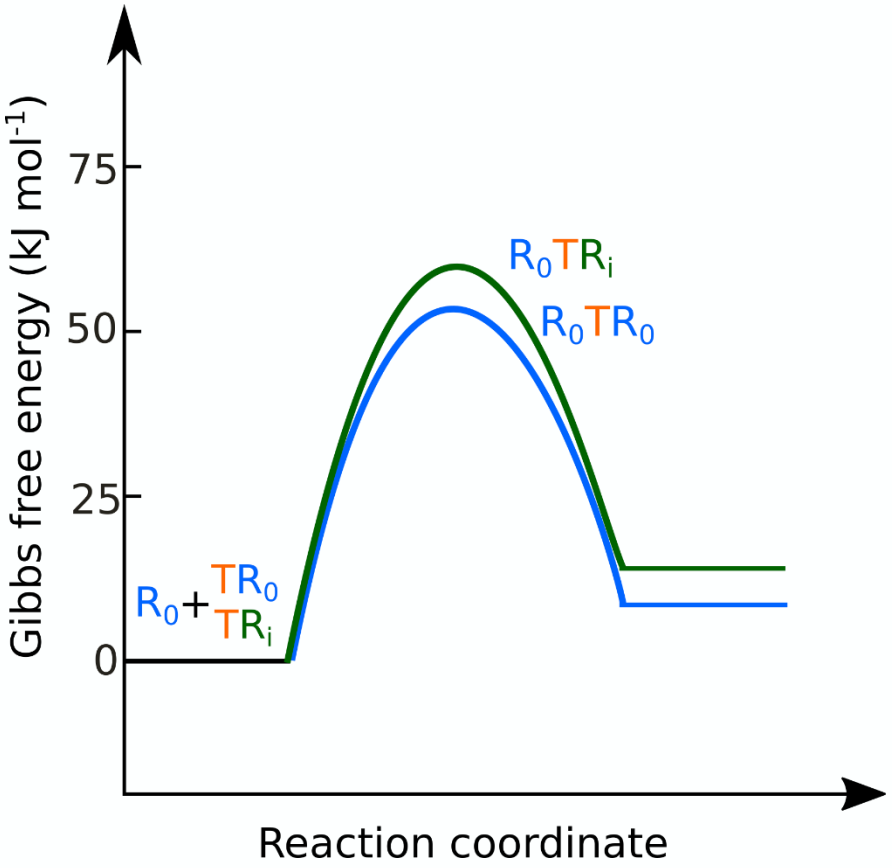
- scan conformers: B3LYP/6-31G(d)
- geometry optimization and frequencies: B3LYP/6-31G(d)
- 'single point' electronic energy: M06-2X/6-311+G(d,p)

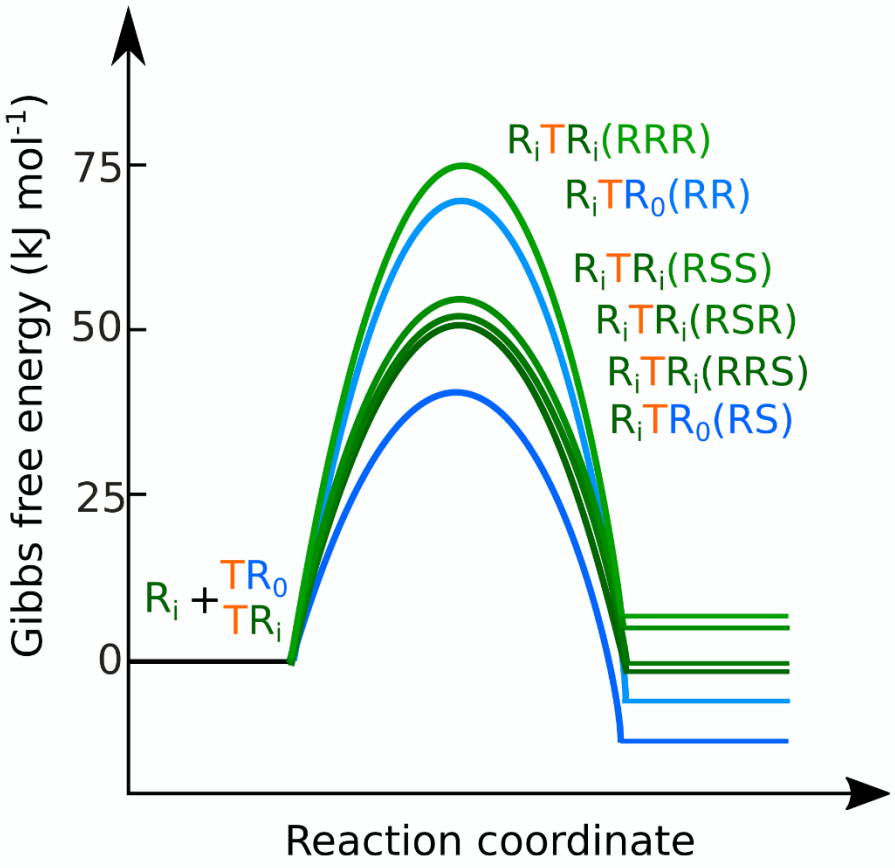
Solvation via COSMO-RS



[a] Lin and Coote, *Aust. J. Chem.* 2011, *94*, 747

Gibbs free energy diagrams of the addition-fragmentation reactions





- Rate coefficients are obtained via classical transition state theory:

$$K = e^{\frac{-\Delta_r G^\circ}{RT}} \qquad k_+ = \frac{k_B T}{h} e^{\frac{-\Delta^\ddagger G^\circ}{RT}} \qquad k_- = k_+ / K$$

- Stereoisomers are taken into account according to the following formulas:

$$k_{add} = \frac{1}{n_0} \sum_i k_{add,i} \qquad k_{frag} = \frac{\sum_i k_{frag,i} K_i}{\sum_i K_i}$$

Deterministic kinetic model based on methods of moments[a]

	Reaction	Equation	E_a kJ mol^{-1}	A L mol^{-1} s^{-1}
FRP	Dissociation*	$I_2 \rightarrow 2R_0$	129.0	1.6 E +15[d]
FRP	(Re)Initiation	$R_0 + M \rightarrow R_1$	26.0	4.9 E +07[e]
FRP	Propagation	$R_i + M \rightarrow R_{i+1}$	32.5	4.2 E +07[f]
FRP	Combination**	$R_i + R_j \rightarrow R_{i+j}$	0.0	5.0 E +08[g]
RAFT	Addition	$R_0 + TR_0 \rightarrow R_0TR_0$	13.9	7.4 E +06
RAFT	Addition	$R_0 + TR_i \rightarrow R_0TR_i$	24.2	1.6 E +07
RAFT	Addition	$R_i + TR_0 \rightarrow R_iTR_0$	3.0	9.4 E +06
RAFT	Addition	$R_i + TR_i \rightarrow R_iTR_i$	15.4	1.7 E +07
RAFT	Fragmentation	$R_0TR_0 \rightarrow R_0 + TR_0$	44.6	9.4 E +12
RAFT	Fragmentation	$R_0TR_i \rightarrow R_0 + TR_i$	48.3	1.2 E +13
RAFT	Fragmentation	$R_iTR_0 \rightarrow R_i + TR_0$	51.7	2.6 E +12
RAFT	Fragmentation	$R_iTR_i \rightarrow R_i + TR_i$	53.2	1.2 E +13

* Initiator efficiency[b]

$$f_{app} = \frac{D_I}{D_I + D_{term}}$$

** Diffusional limitations

Via **composite k_t model**[c]

- for $i < i_{gel}$ and $i < i_{SL}$:

$$k_{t,ii}^{app} = k_{t,11} i^{-\alpha_s}$$

- for $i < i_{gel}$ and $i \geq i_{SL}$:

$$k_{t,ii}^{app} = k_{t,11} i_{SL}^{\alpha_l - \alpha_s} i^{-\alpha_l}$$

- for $i \geq i_{gel}$ and $i < i_{SL}$:

$$k_{t,ii}^{app} = k_{t,11} i_{gel}^{\alpha_{gel} - \alpha_s} i^{-\alpha_{gel}}$$

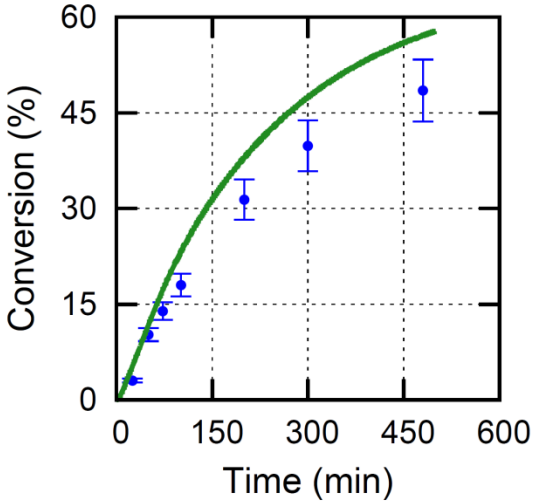
- for $i \geq i_{gel}$ and $i \geq i_{SL}$:

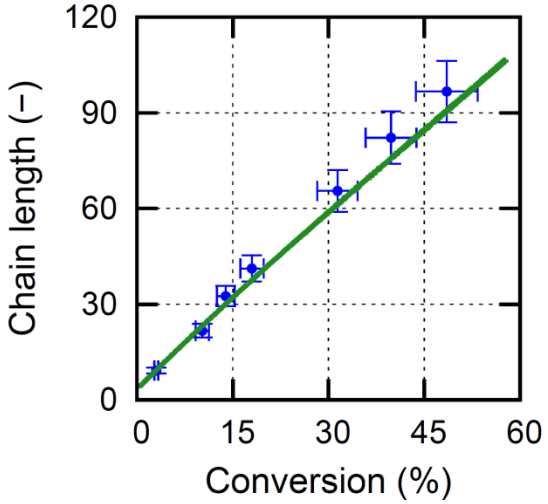
$$k_{t,ii}^{app} = k_{t,11} i_{SL}^{\alpha_l - \alpha_s} i_{gel}^{\alpha_{gel} - \alpha_l} i^{-\alpha_{gel}}$$

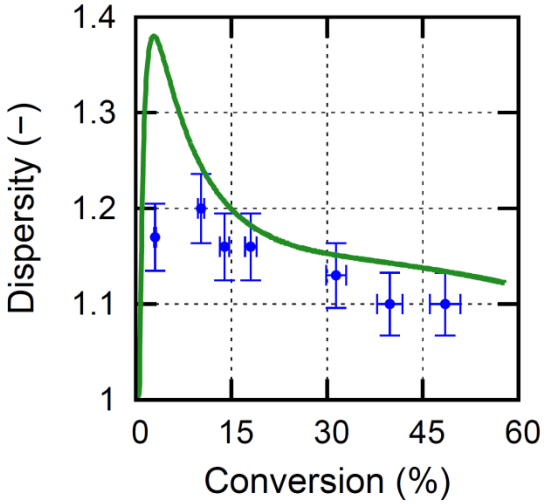
[a] De Rybel *et al.*, *Macromol. Theor. Simul.* 2016, *in press;* [b] Buback *et al.*, *Macromol. Chem. Phys.* 1994, *195*, 2117; [c] Johnston-Hall and Monteiro, *J. Polym. Sci. Polym. Chem.* 2008, *46*, 3155-3173; [d] Van Hook el al, *J. Am. Chem. Soc.* 1958, 80, 779–782; [e] Hėberger el al., *Int. J. Chem. Kinet*. 1993, 25, 249–263; [f] M. Buback, *Macromol. Chem. Phys.* 1995, 196, 3267–3280; [g] Johnston-Hall et al., *Macromolecules,* 2008, 41, 727–736

Simulation and experimental validation

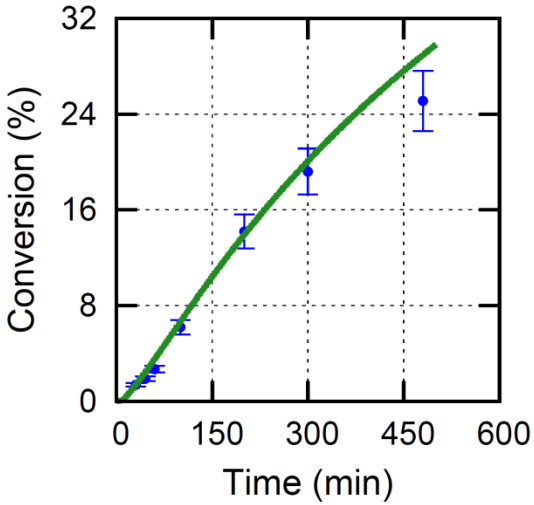
T = 80 °C, TCL = 200, CTA:AIBN = 5:1

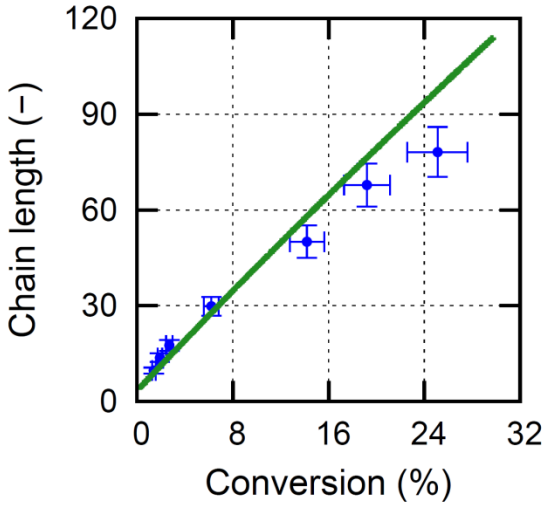


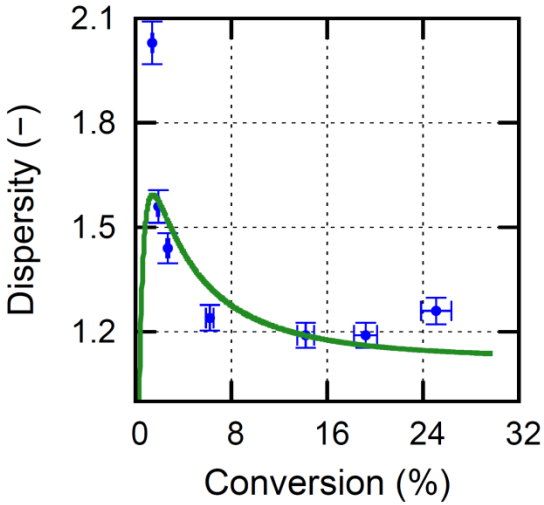




T = 70 °C, TCL = 400, CTA:AIBN = 5:1







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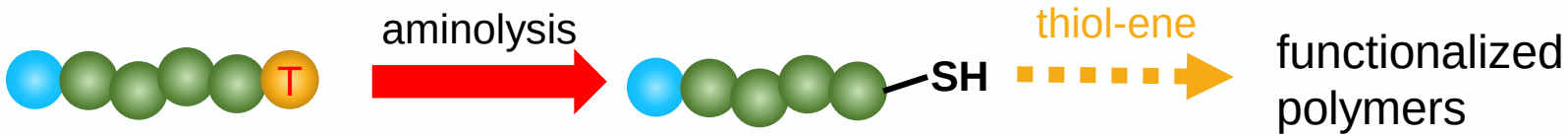
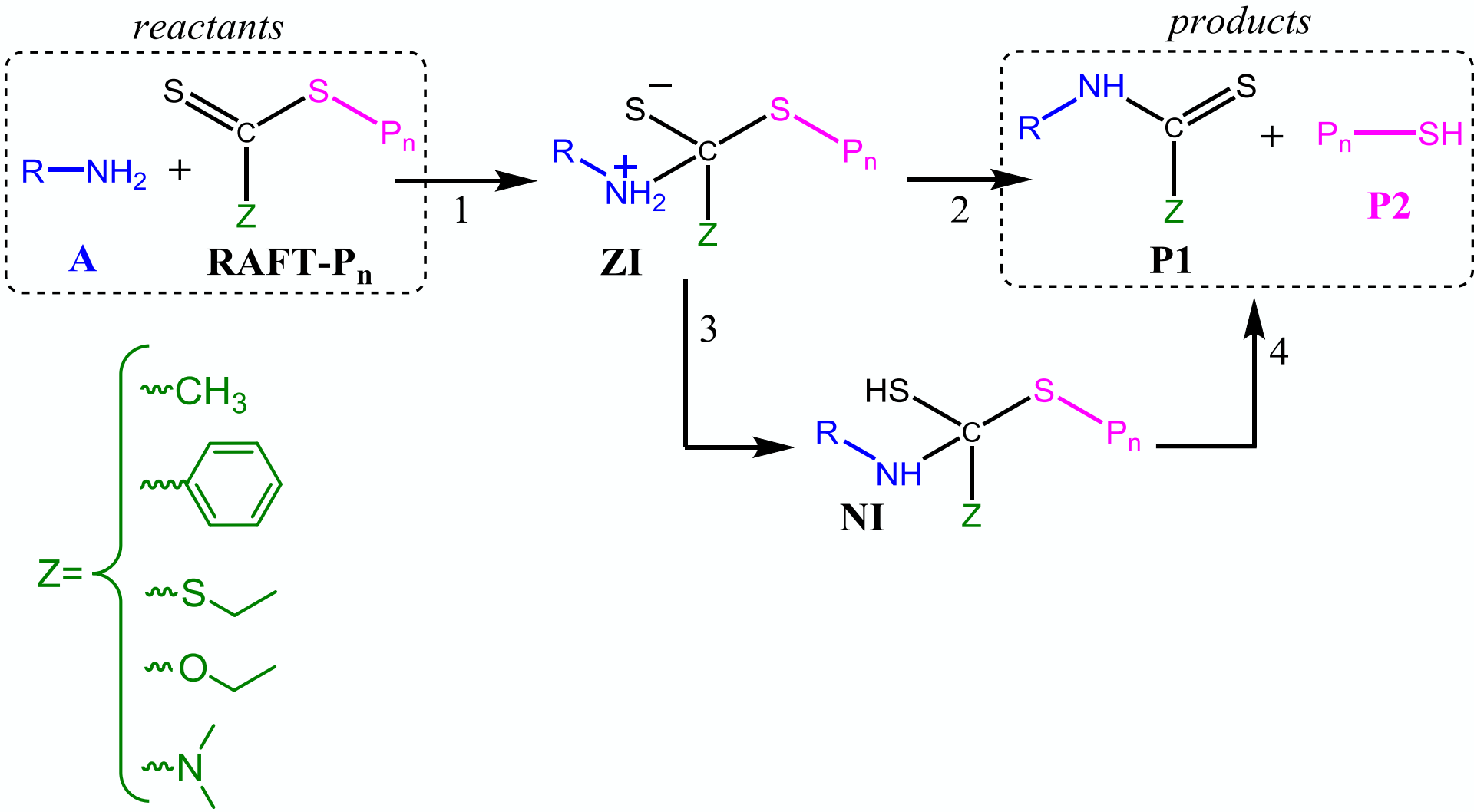
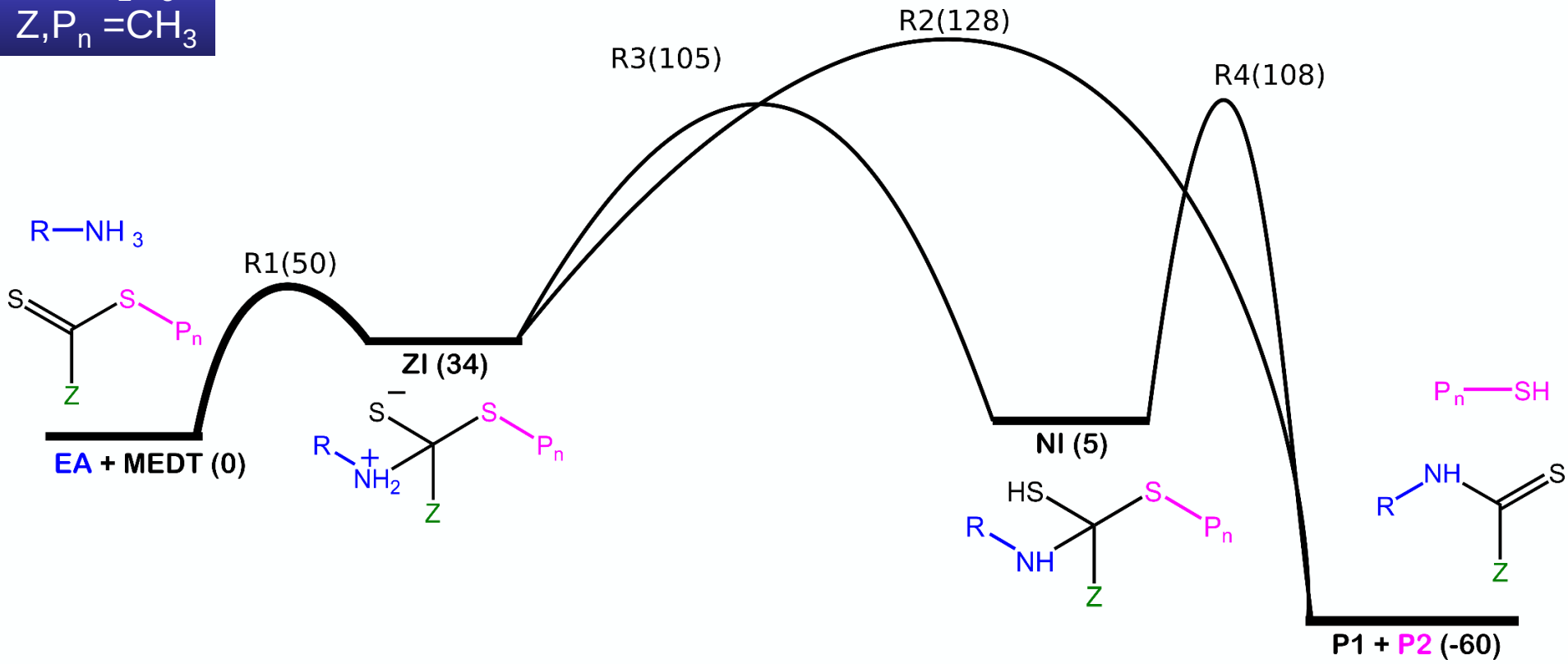


Aminolysis of RAFT agents in aprotic solvents: reaction mechanism



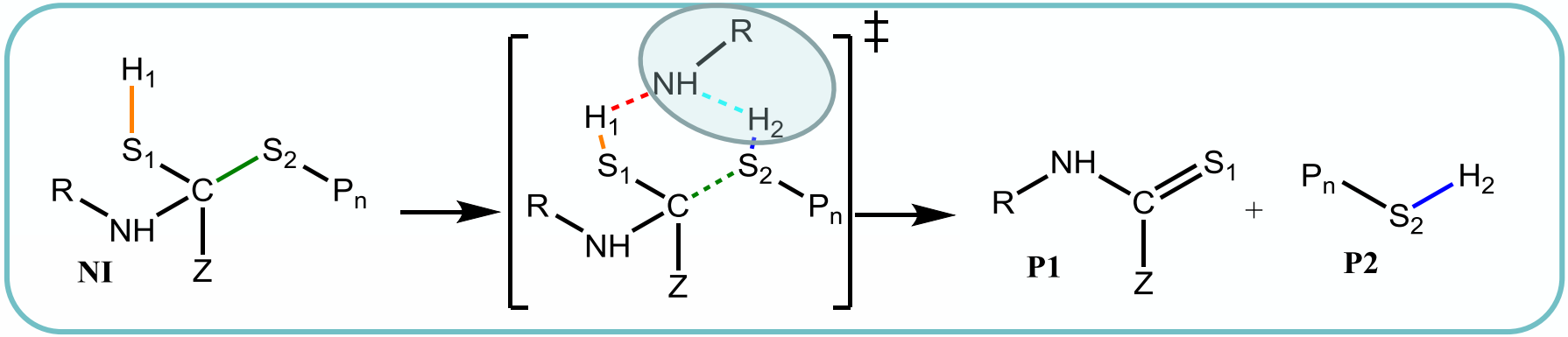
Gibbs Free Energy Diagram for EthylAmine (EA) + Methyl Ethane DiThioate (MEDT)

$R = C_2H_5$
$Z,P_n = CH_3$



(Gibbs free energies in kJ mol^{-1} at 298.15 K)

Amine assisted transition state are asynchronous and early



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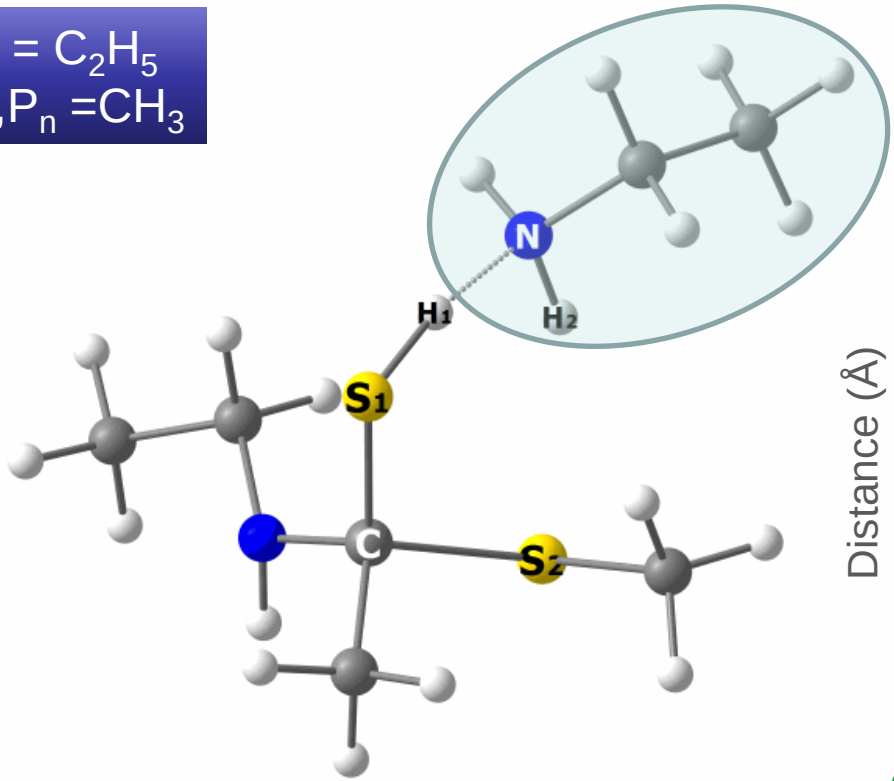
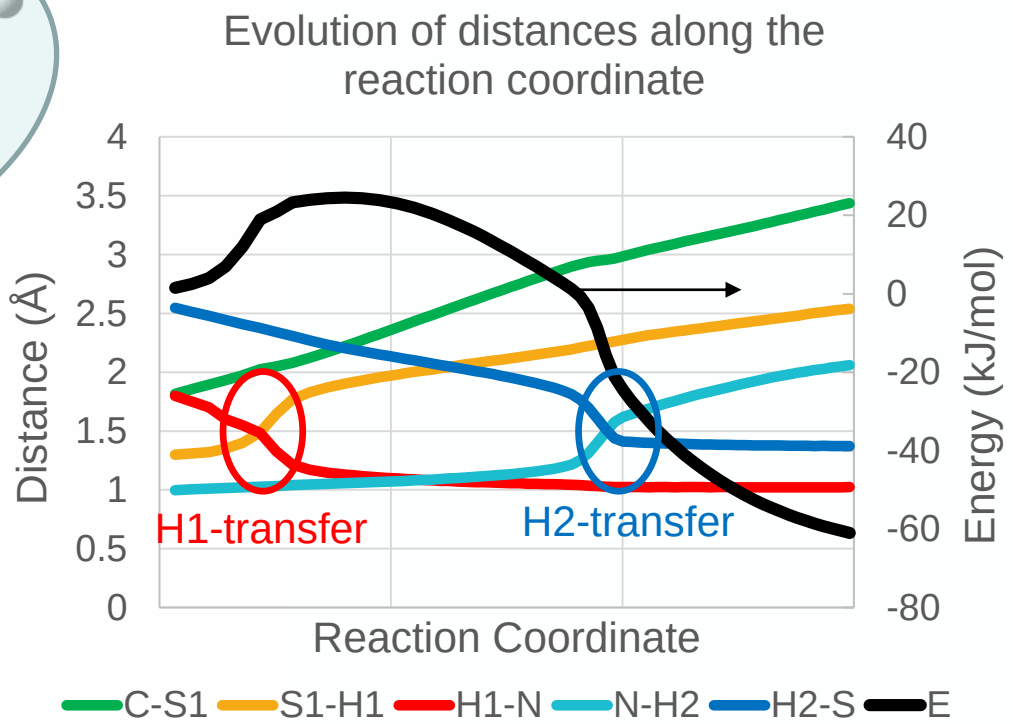
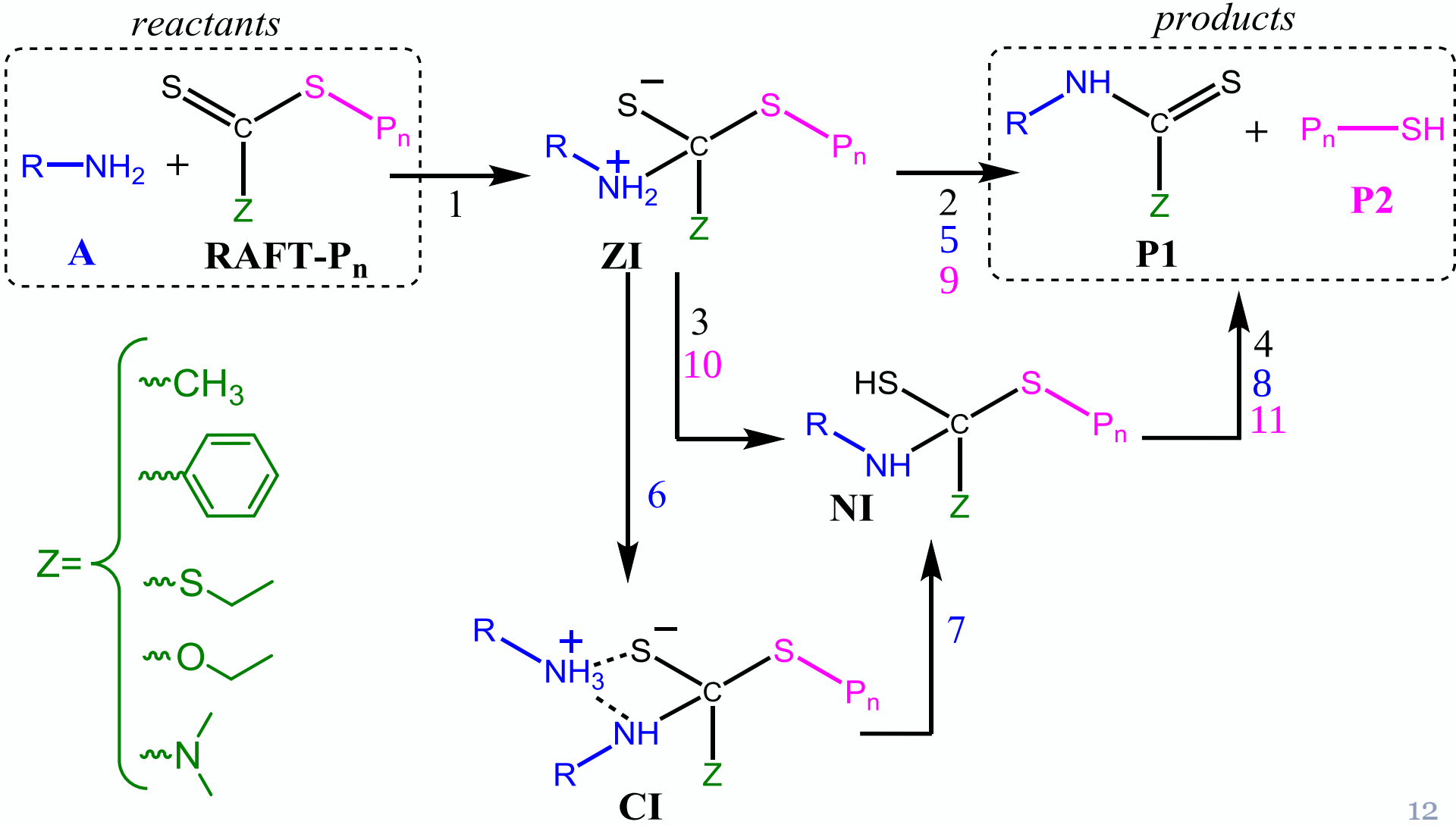


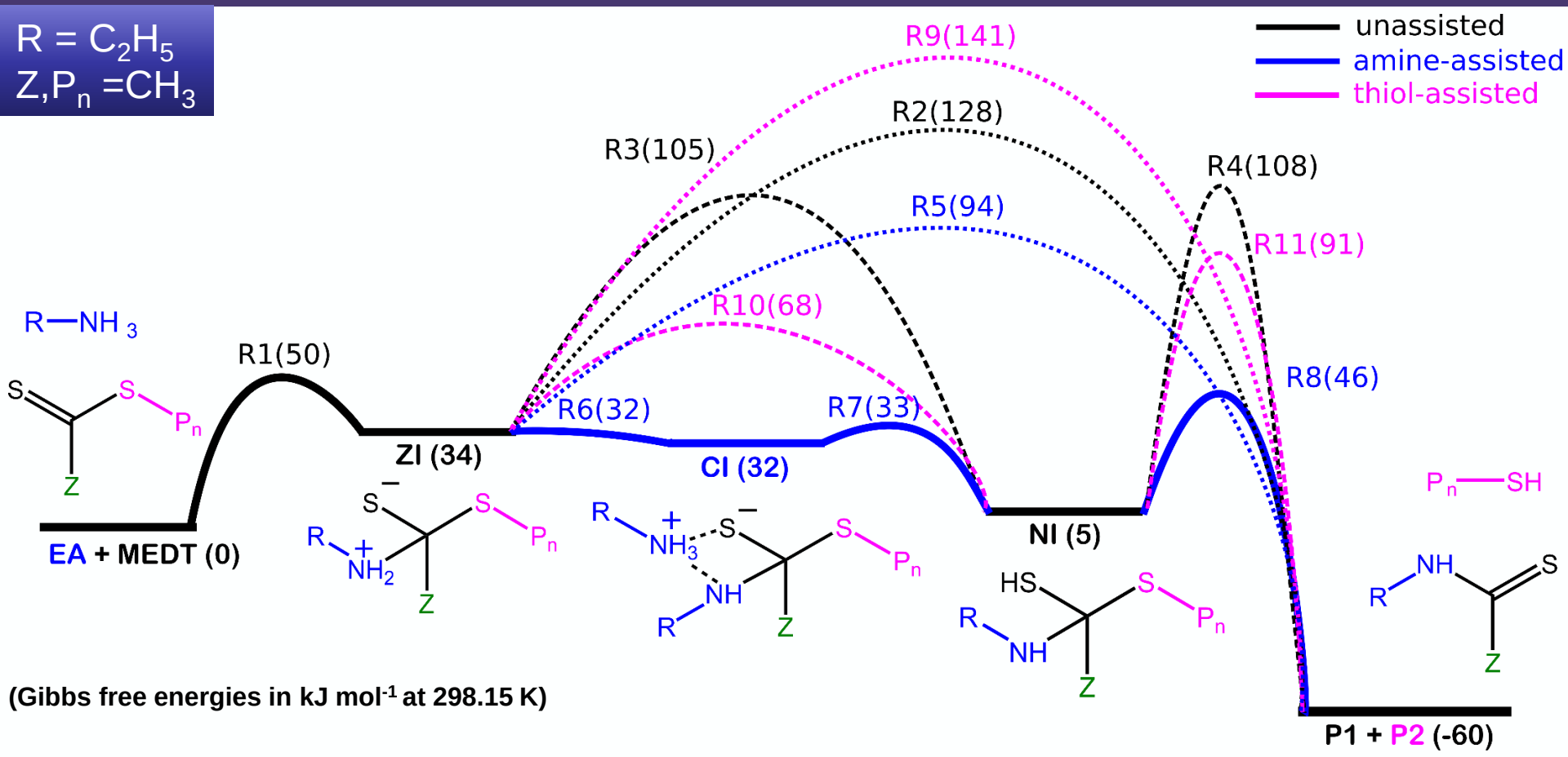


Aminolysis of RAFT agents in aprotic solvents: reaction mechanism

- Proton transfer in transition states can be assisted by amines and by thiols



Gibbs Free Energy Diagram for EthylAmine (EA) + Methyl Ethane DiThioate (MEDT)

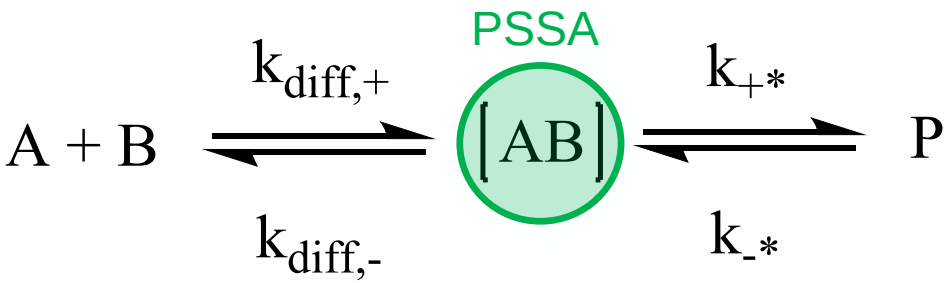


	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11
k_+	**1.3E+04**	2.3E-04	2.4E+00	4.3E-06	2.2E+02	**6.2E+12**	**5.6E+12**	**3.4E+05**	1.1E-06	7.8E+06	4.0E-03
k_-	**1.3E+10**	7.5E-21	1.5E-05	2.2E-17	7.2E-15	**7.0E+12**	**7.6E+07**	**1.8E-06**	3.6E-23	5.0E+01	2.1E-14

(k_+ and k_- in L mol^{-1} s^{-1} or s^{-1})

diffusional limitations become important!

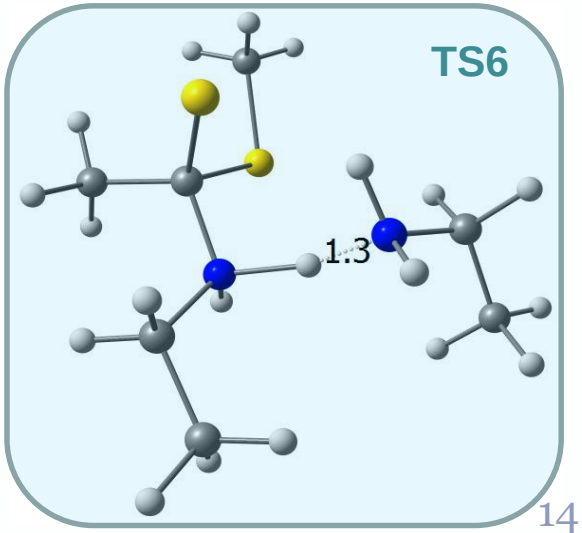
The coupled encounter pair model to account for diffusion for TS 6 and 7



$$\frac{1}{k_{app,+}} = \frac{1}{k_{+}} + \frac{1}{k_{diff,+}}$$

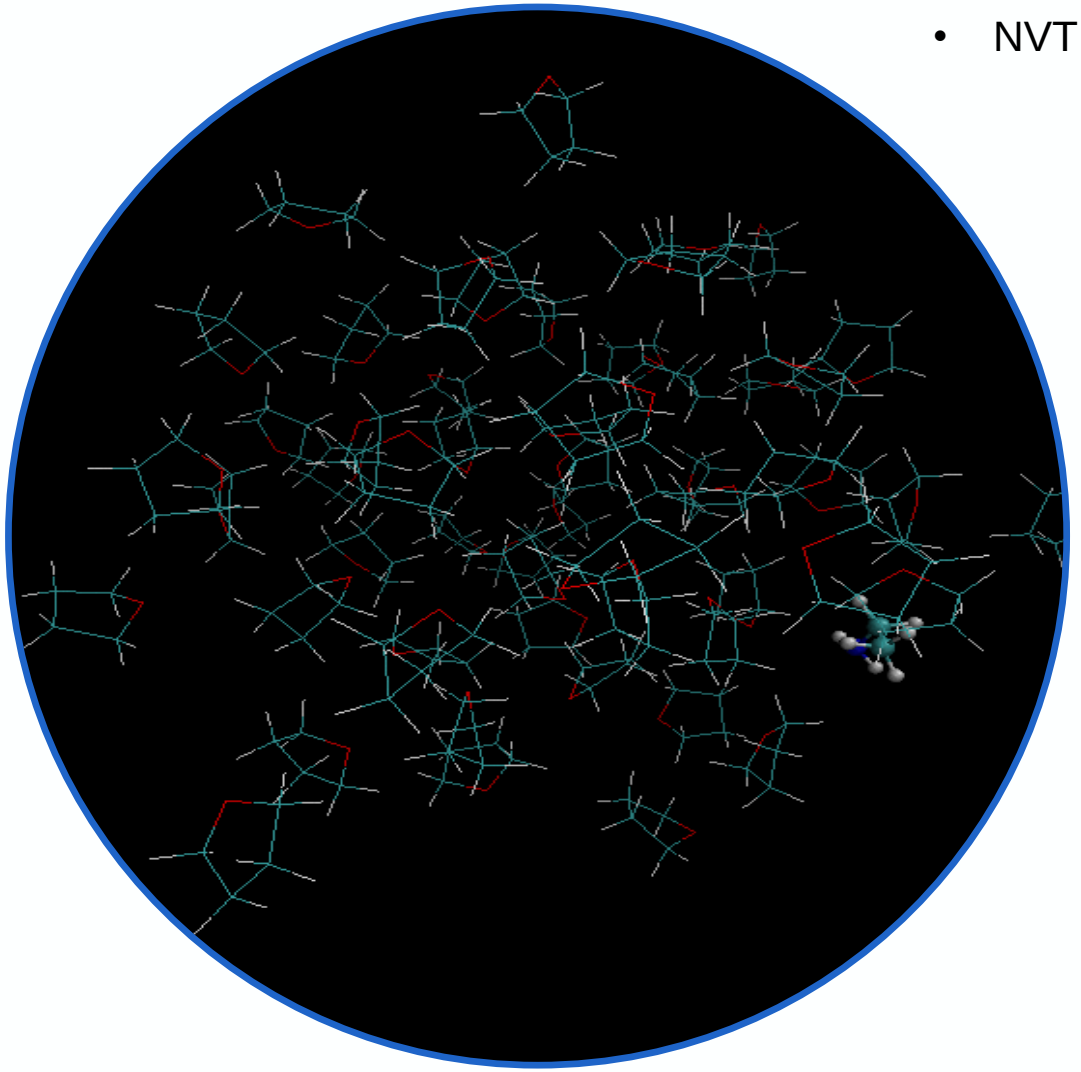
$$\frac{1}{k_{app,-}} = \frac{1}{k_{-}} + \frac{K}{k_{diff,+}}$$

- Diffusion of A+B towards [AB] via the model of **Smoluchowski**: $k_{diff} = 4\pi N_A \sigma D_{AB}$
  - σ = reaction distance: from ab initio TS geometries
  - D_{AB} = mutual diffusivity coefficient[a] $D_{AB} = \frac{D_A, D_B}{D_{solvent}}$ MD

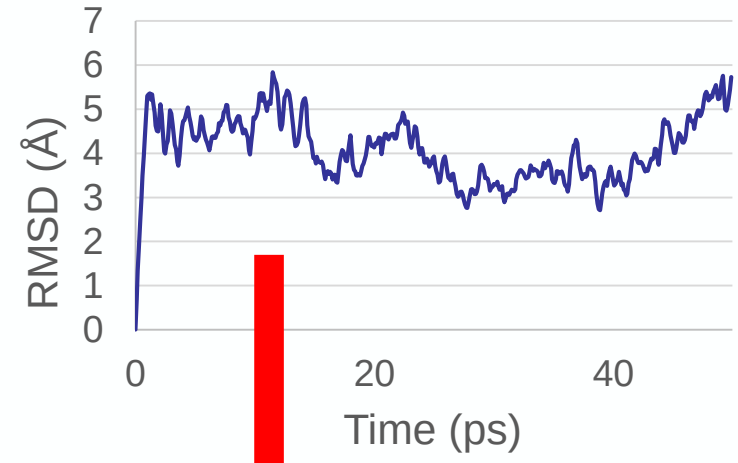


[a] Liu et al. *Ind Eng Chem Res* **2011**, *50*, 4776.

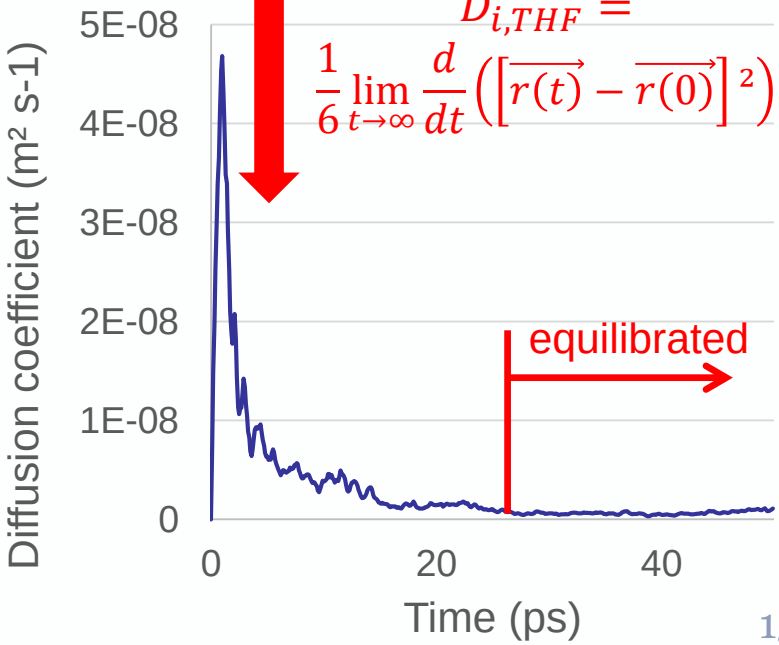
Diffusivity coefficients based on molecular dynamics



- NVT ensemble in 8 nm^3 box for 50 picoseconds

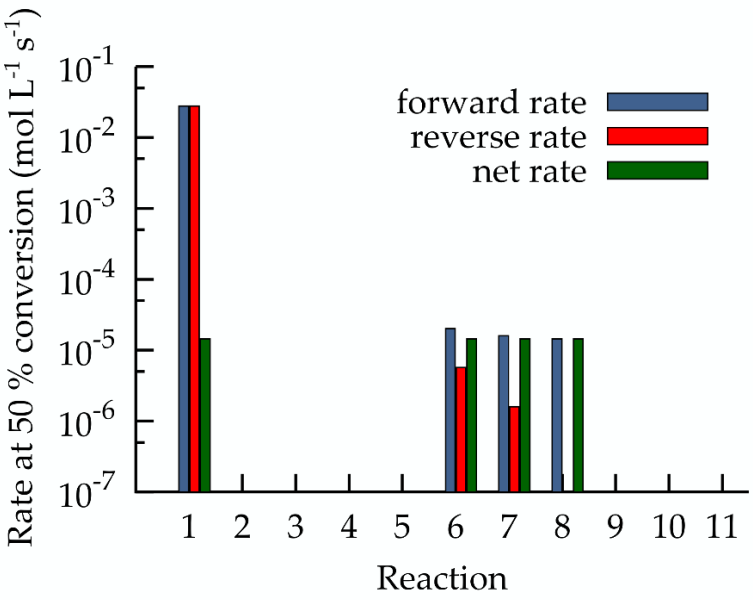


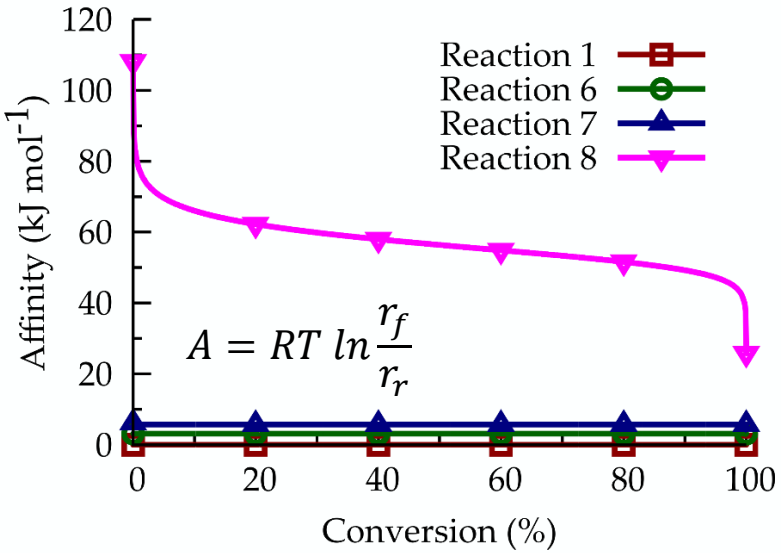
$$D_{i,THF} = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\left(\left[\overrightarrow{r(t)} - \overrightarrow{r(0)}\right]^2\right)$$



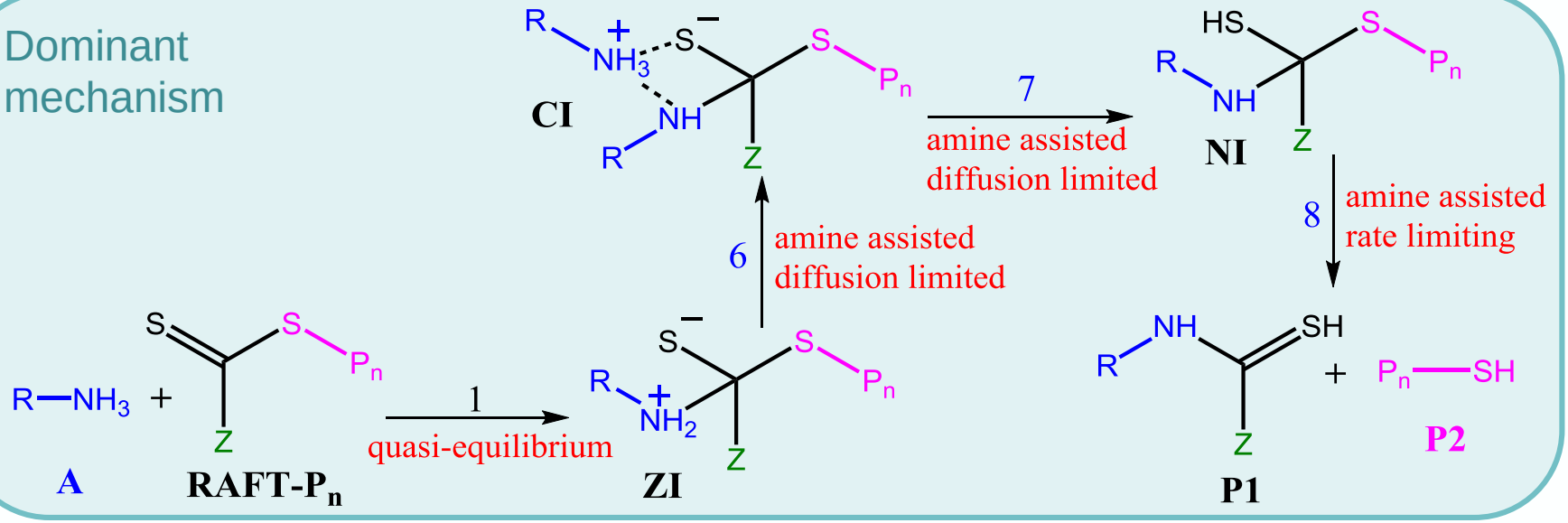
	k_+	k_{diff}	$k_{app,+}$
R6	6.2E+12	2.1E+09	2.1E+09

Rate and affinity analysis reveal the dominant path and the nature of the elementary steps for the aminolysis of MEDT



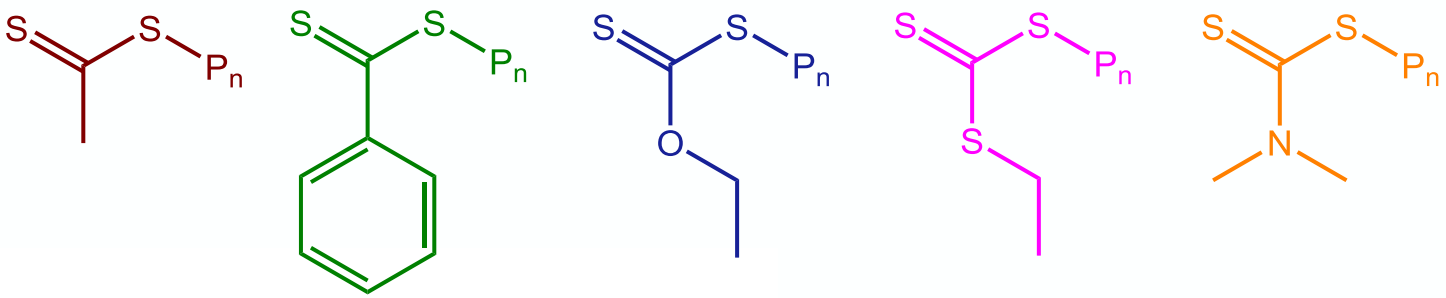


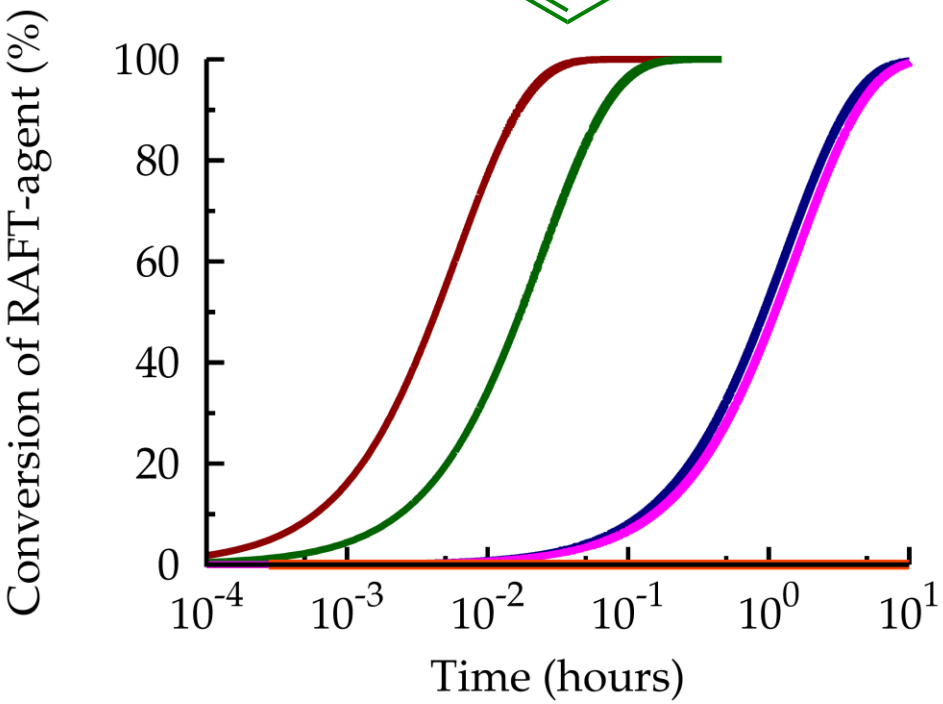
Dominant mechanism



Prediction of conversion profiles for other RAFT-agents

Reaction of 10^{-3} mol L^{-1} RAFT-macromolecule with 5 x 10^{-3} mol L^{-1} ethylamine in THF at 25 °C for dithioates, thiobenzoates, xanthates, trithiocarbonates and dithiocarbamates:





- dithiocarbamates are not reactive at room temperature! (in agreement with experiment observations[a])
- conversion of xanthates and dithiobenzoates show good agreement with literature[b] (<factor 2)
- reaction of trithiocarbonates slower than xanthates[b]

[a] Le Neindre et al, Polym Chem **2013**, 4, 5577
[b] Kabachii et al, *Pol Sci Ser A* **2006,** 48, 717

Conclusion: first principles techniques are a valuable tool to obtain reaction parameters for kinetic models

1. **RAFT polymerization** of styrene with a trithiocarbonate
   - Calculation of **addition-fragmentation** rate coefficients
   - Implementation in microkinetic model
     - conversions
     - chain lengths
     - dispersities
2. **Aminolysis** of RAFT-macromolecules
   - Determining the **dominant mechanism** using ab initio based kinetic model
     - **quasi-equilibrated formation of a zwitterion**
     - **amine-assisted diffusion-limited proton transfer** over a complex intermediate towards a neutral intermediate
     - rate limiting amine-assisted breakdown of the neutral intermediate towards the product
   - Simulation of conversion of range of RAFT agents
     - Reactivity: thioates > thiobenzoates > xanthates ≥ trithiocarbonates >> dithiocarbamates

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- LCT colleagues

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belspo

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Questions?