

# Kinetic Modeling Explains Inherent Limitations of Radical Thiol-Ene Chemistry for Macromolecular Design

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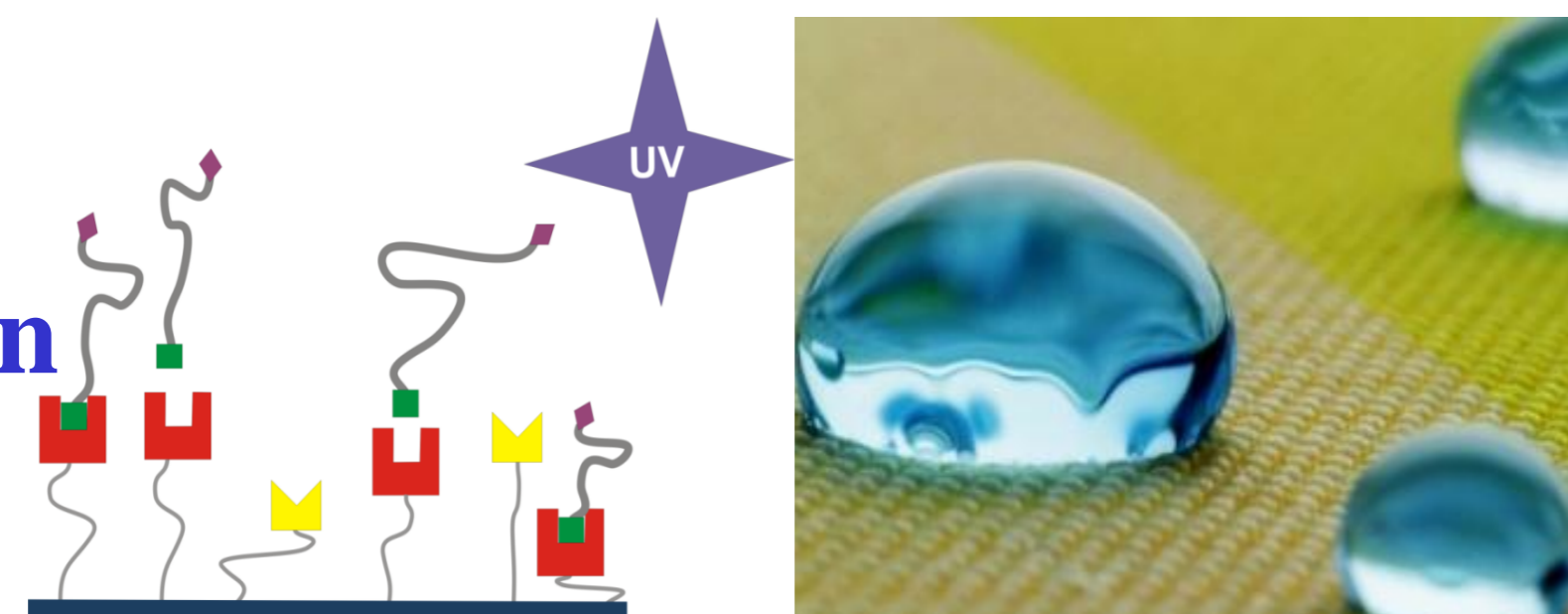
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## INTRODUCTION

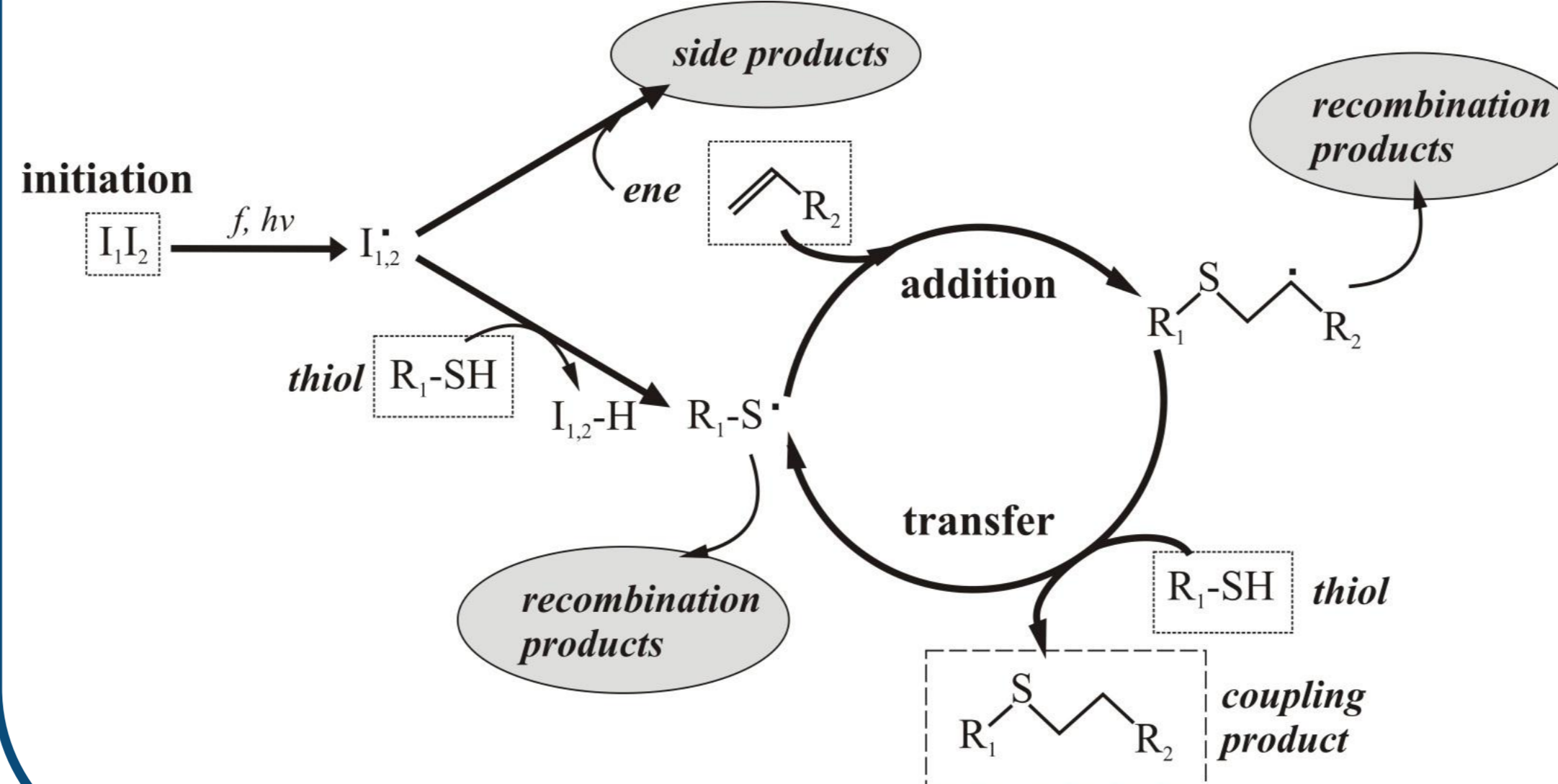
Ever since Sharpless et al.<sup>[1]</sup> introduced the concept of “click” chemistry, many reactions have been explored as possible “click” reactions. In particular radical thiol-ene coupling reactions are highlighted as a very promising alternative to the Cu catalyzed azide-alkyne click reaction (CuAAC), since these reactions can be performed in the presence of UV light without a (toxic) catalyst, leading to a wide range of applications, e.g.

### Polymer modification



<sup>[1]</sup> H.C. Kolb, M.G. Finn, K.B. Sharpless, *Angewandte Chemie*, 2001, 40 (11), 2004

## REACTION SCHEME



## SCOPE

Systematic experimental study (FTIR, <sup>1</sup>H-NMR, GC; λ=360 nm)

intrinsic rate coefficients low molar mass system: DVE/BT/DMPA/1,4-dioxane

Modeling study small-small, polymer-small, polymer-polymer

Reduced coupling efficiency with macromolecular species<sup>[2]</sup>

DVE = dodecyl vinyl ether  
BT = benzyl thiol  
DMPA = 2,2-dimethoxy-2-phenyl acetophenone  
PS-SH = thiol-functionalized polystyrene prepared by RAFT polymerization

Kinetic model

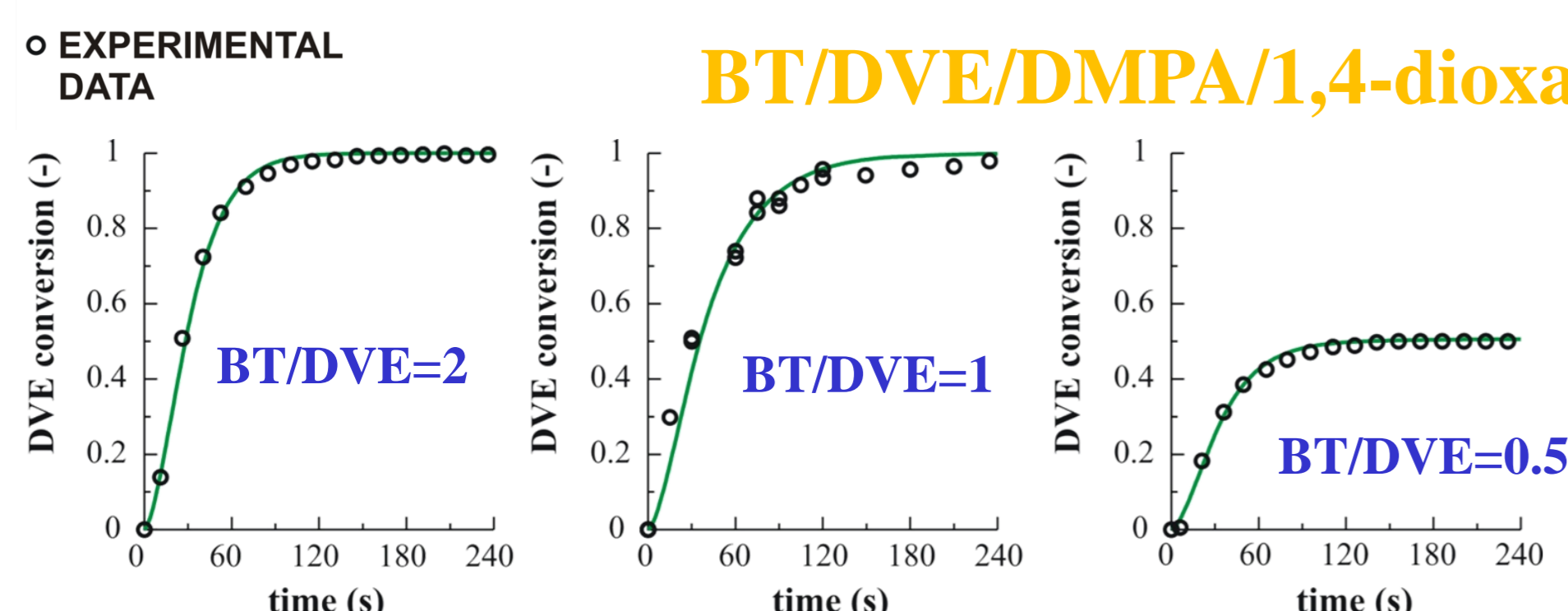
Effect diffusional limitations + (initiator-derived) side reactions

<sup>[2]</sup> Koo S.P.S. et al., *J. Polymer Science: Part A: Pol. Chemistry*, 2010, 48, 1699-1713

## KINETIC MODELING RESULTS: SMALL-SMALL

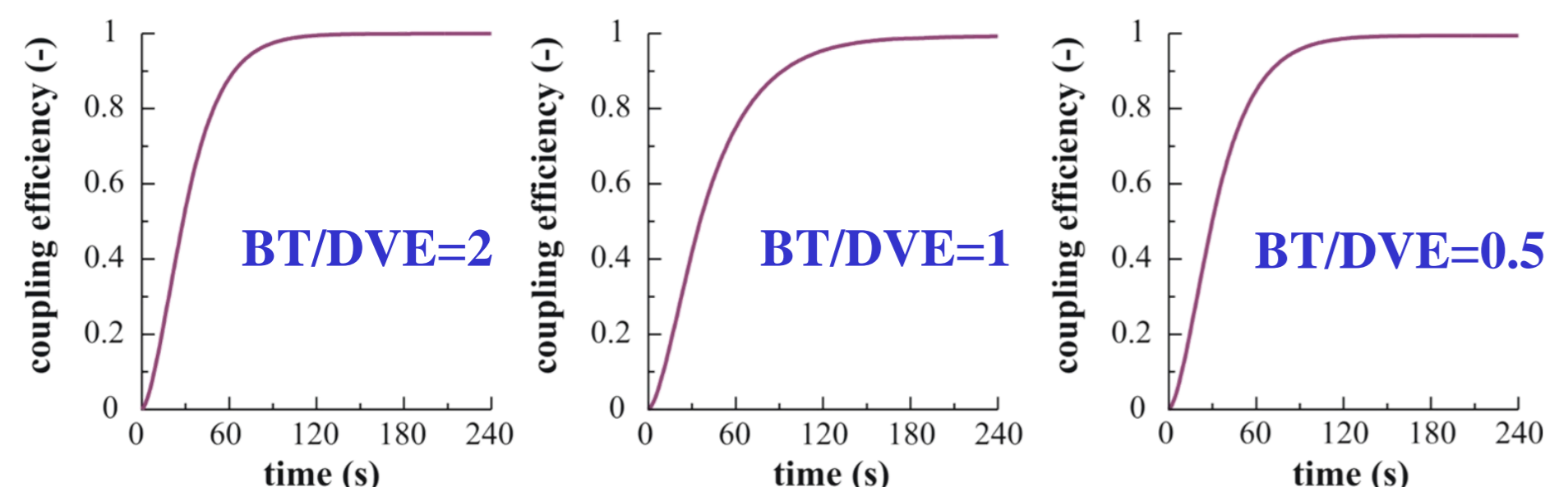
### INTRINSIC KINETICS<sup>[3]</sup>

#### BT/DVE/DMPA/1,4-dioxane:

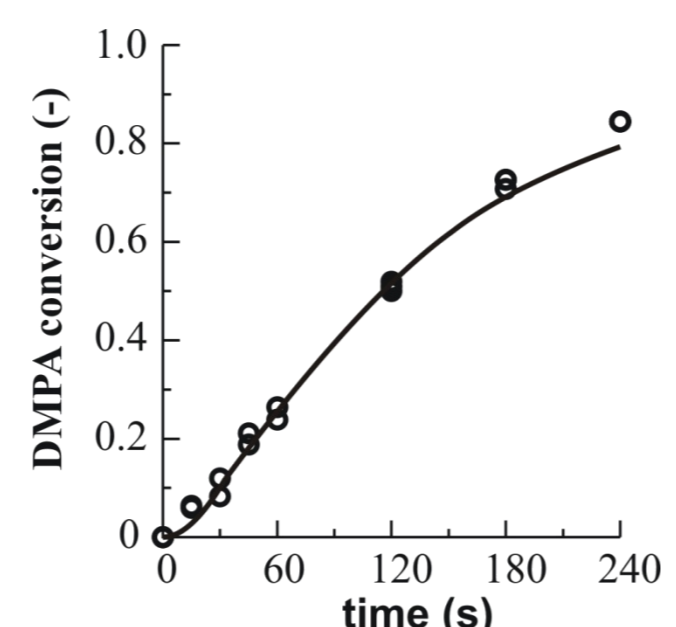


Intrinsic chemical rate coefficients:  
 $k_p = 1.2 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$   
 $k_{CT} = 1.1 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$

#### Good agreement



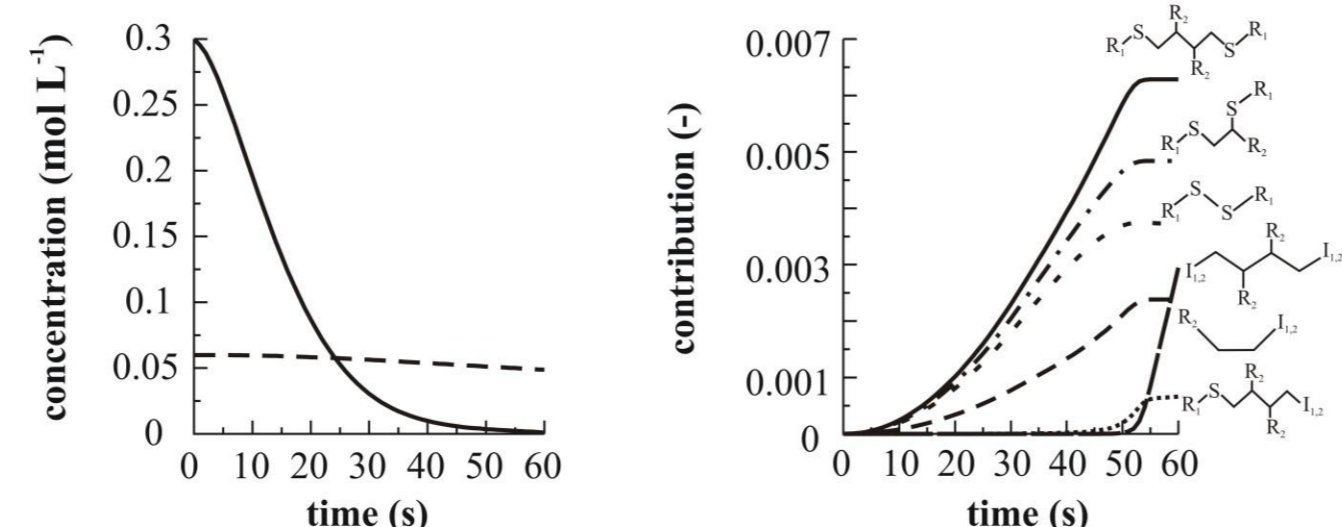
#### Good agreement DMPA conversion



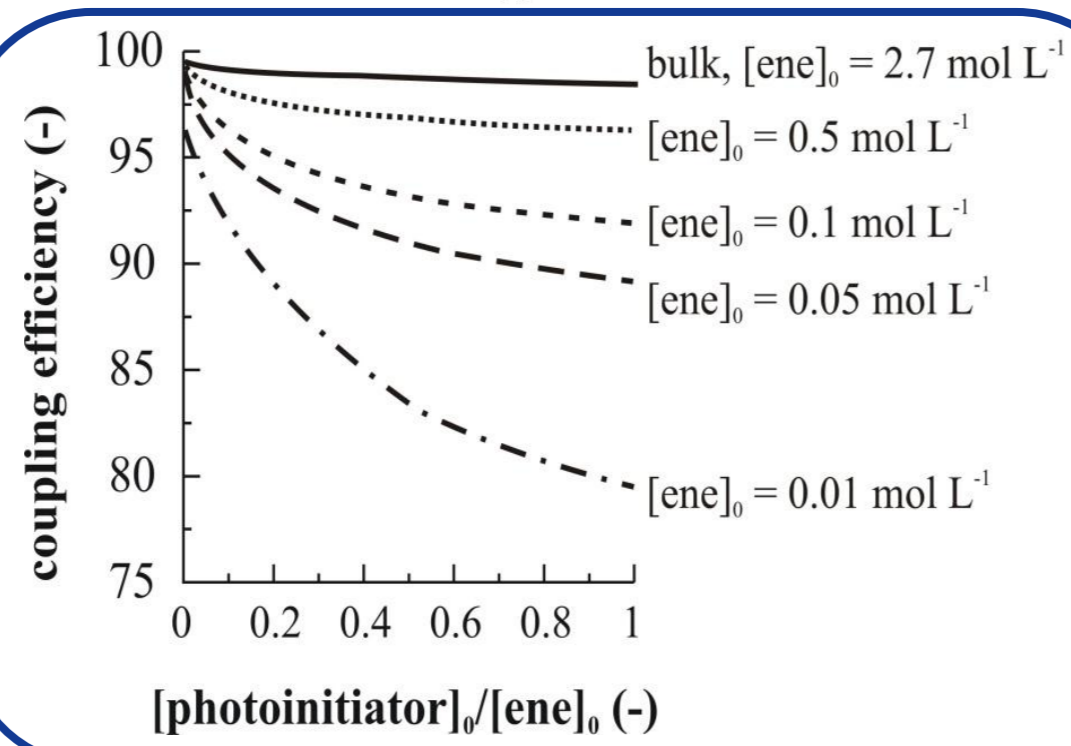
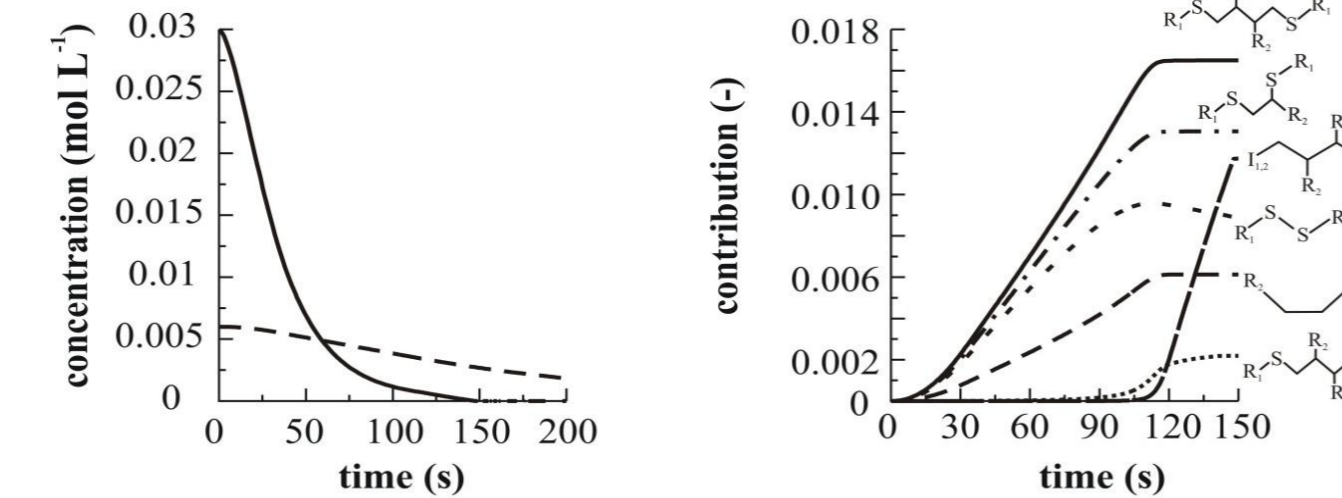
$$f_{\text{coupling}} = \frac{[\text{thio-ether}]}{[\text{RSH/R'CH=CH}_2]_0} \sim 100\%$$

Only for present conditions  
Pronounced influence concentrations on  $f_{\text{coupling}}$

#### small-small conditions



#### polymer-polymer conditions

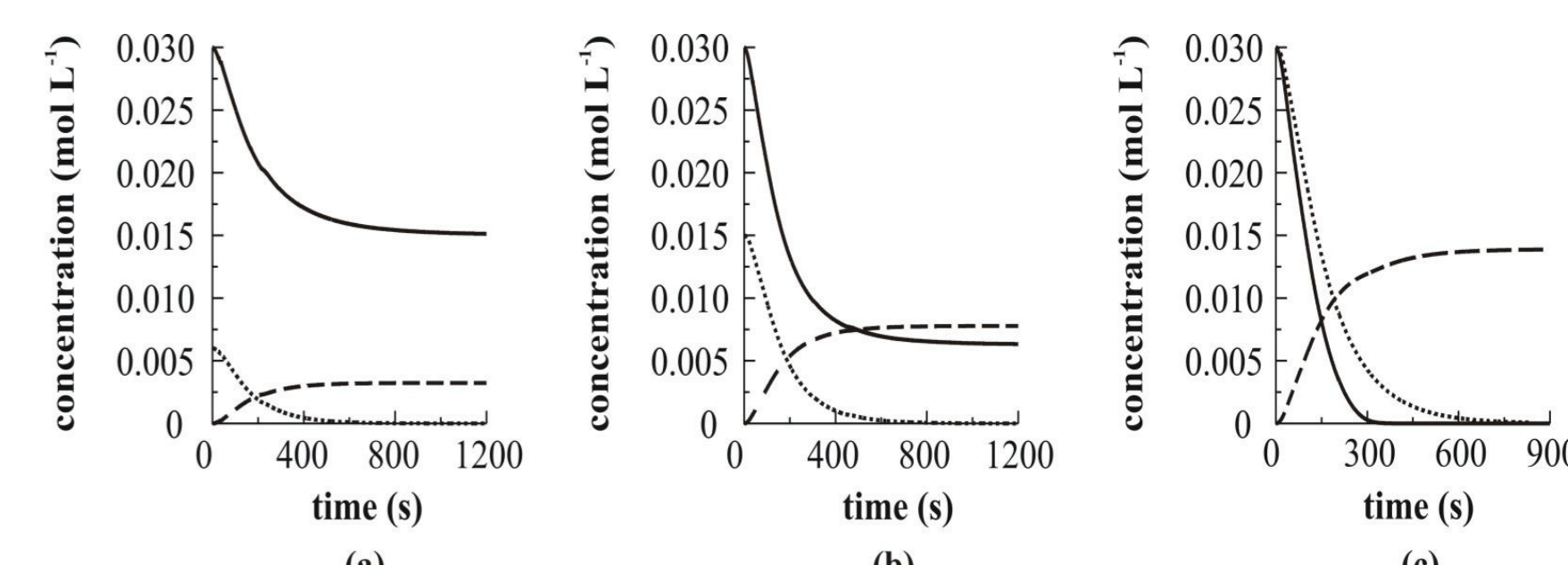


Decrease of  $f_{\text{coupling}}$  for lower  $c_{\text{ene}}$  or  $c_{\text{thiol}}$  and higher  $c_{\text{photoinitiator}}$

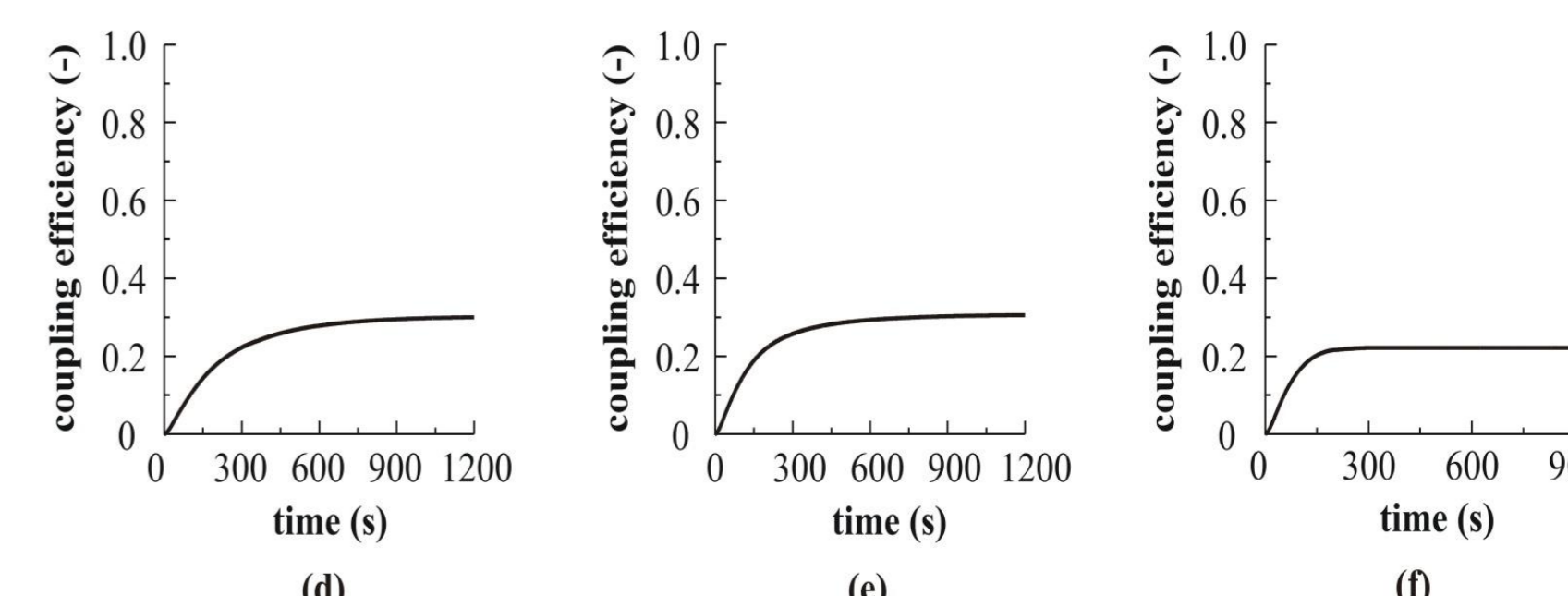
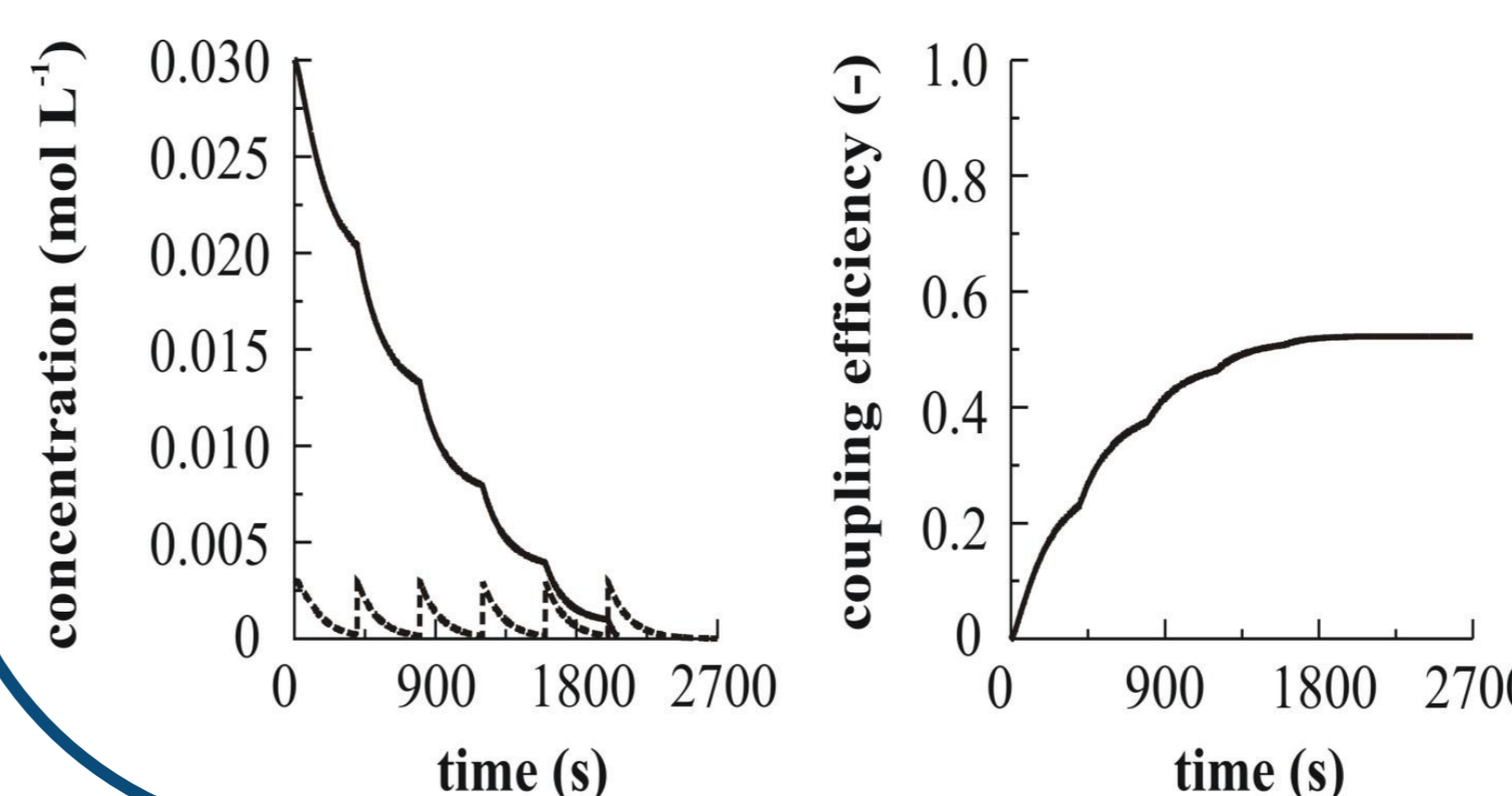
## KINETIC MODELING RESULTS: POLYMER-SMALL

### NO “CLICK” CHARACTERISTICS<sup>[3]</sup>

(a/d)  $f_{\text{coupling}}$  in agreement with experiment (~0.25)  
(b,c,e,f) increase of  $c_{\text{photoinitiator}}$  has no effect



### APPARENT RATE COEFFICIENTS $k_{\text{app}}$



Improvement, but  $f_{\text{coupling,max}} = 0.6$  by stepwise addition photoinitiator

<sup>[3]</sup> P. Derboven, D. R. D'hooge, M. M. Stamenovic, P. Espeel, G. B. Marin, F. E. Du Prez, M.-F. Reyniers, *Macromolecules* 2013, 46, 1732-1742

## CONCLUSIONS

Based on the related low molar mass system (DVE/BT/DMPA/1,4-dioxane; BT: benzyl thiol) and a detailed product characterization, approximate kinetic parameter values are determined allowing to assess the importance of side reactions and diffusional limitations for the polymeric radical thiol-ene reactions. It is found that the reduced coupling efficiency for the latter reactions is attributed to recombination reactions and side reactions with DMPA fragments, which highly depend on the initial concentrations. Diffusional limitations are not responsible for the observed limitations.

## ACKNOWLEDGEMENTS

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