Solvent and Temperature Effects in the Photoiniferter RAFT Polymerisation of Poly(Ethylene Glycol) Methacrylate*

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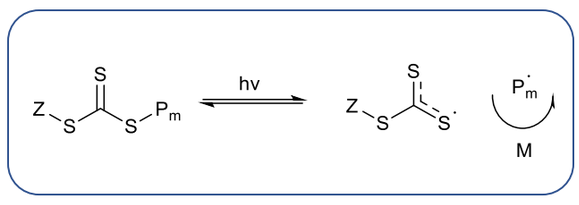
Introduction

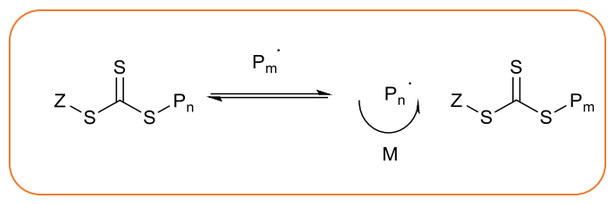
Poly(PEGMA) (PPEGMA) is a bottle-brush homopolymer and a potential biocompatible material. Compared to polyethylene glycol (PEG), its brush confirmation enhanced the stealth properties and non-immunogenicity. [1, 2] Yet, the highly reactive free radical of PEGMA makes control of its polymerisation challenging. Photoiniferter-RAFT polymerization is a promising approach to synthesise a broad range of polymers because of its highly 'living' nature. [3]

We aimed to investigate a better synthetic method for PPEGMA, and investigated the effect of excitation wavelength, intensity, temperature, concentration, and solvents. The effect of solvents on photoiniferter-RAFT hasn't been previously reported.

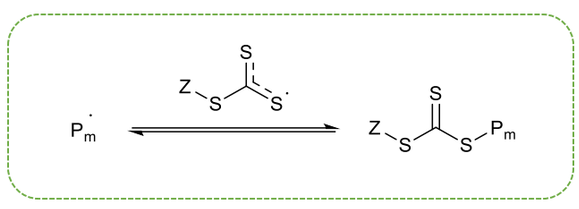
Photoactivation



RAFT Equilibrium

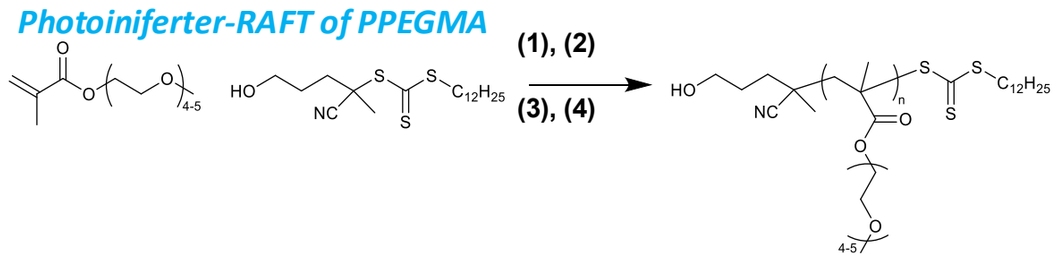


Reversible termination



Scheme 1. General mechanism of photoiniferter-RAFT polymerisation.

Photoiniferter-RAFT of PPEGMA



(1) Wavelength

450 nm
470 nm

515 nm

(2) Concentration

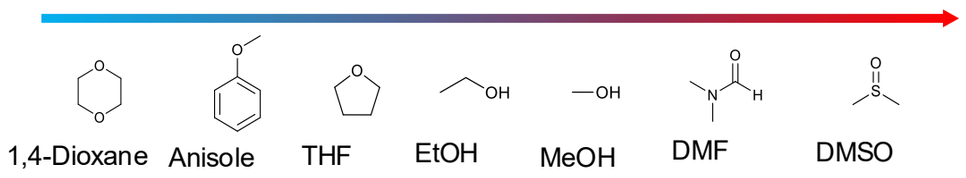
50 %v/v
23 %v/v
17 %v/v
9 %v/v

(3) Intensity

18 mW/cm²
1.6 mW/cm²

(4) Solvents & Temperatures

Dielectric constant



1,4-Dioxane	Anisole	THF	EtOH	MeOH	DMF	DMSO
37 ˚C 33 ˚C 22 ˚C	40 ˚C 25 ˚C 12 ˚C					40 ˚C 31 ˚C 25 ˚C

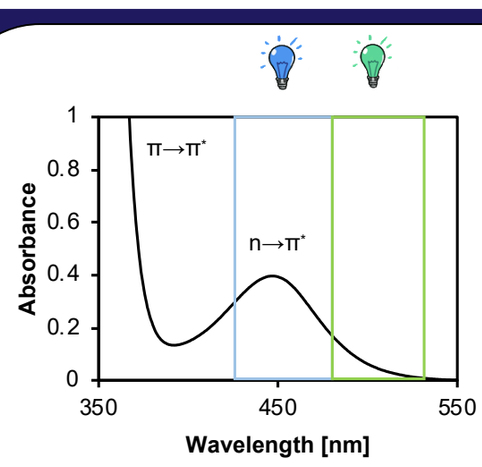


Fig 1. Absorbance of CTA in DMSO

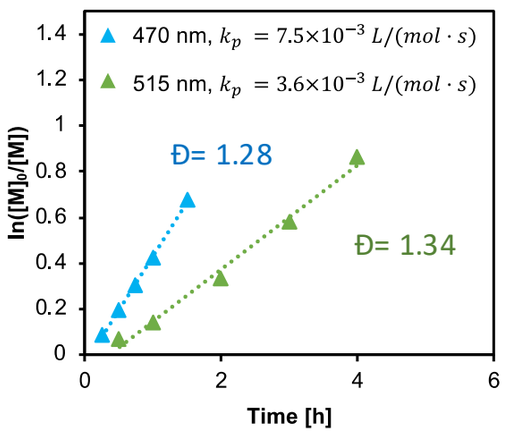
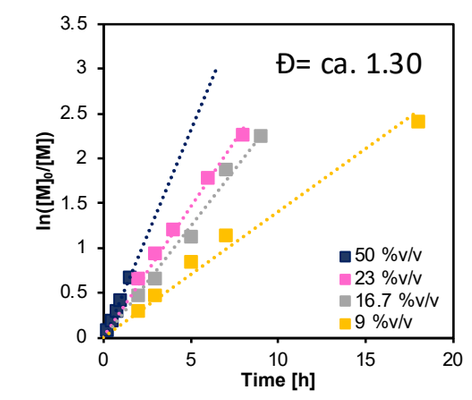


Fig 2. Polymerization kinetics. λ_{max} = 470 and 515 nm, 1.6 mW/cm² in DMSO, 50 %v/v, 22 °C.



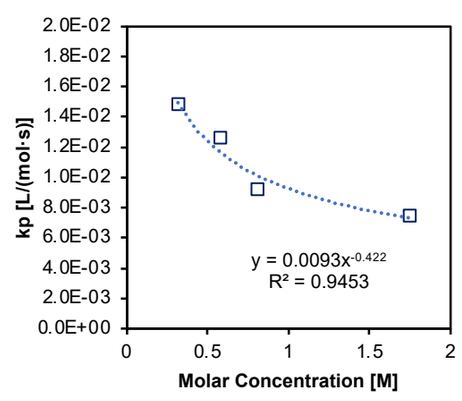


Fig 3. Polymerization kinetics at 50, 23, 17, and 9 %v/v in DMSO. Initiated under λ_{max} = 470 nm, 1.6 mW/cm² in DMSO, 22 °C.

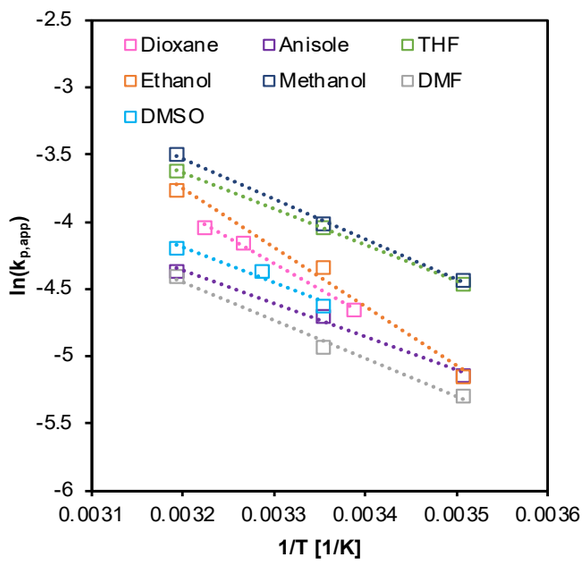


Fig 4. Arrhenius plot for various solvents. λ_{max} = 450 nm, 18 mW cm^{-2}, 50 %v/v.

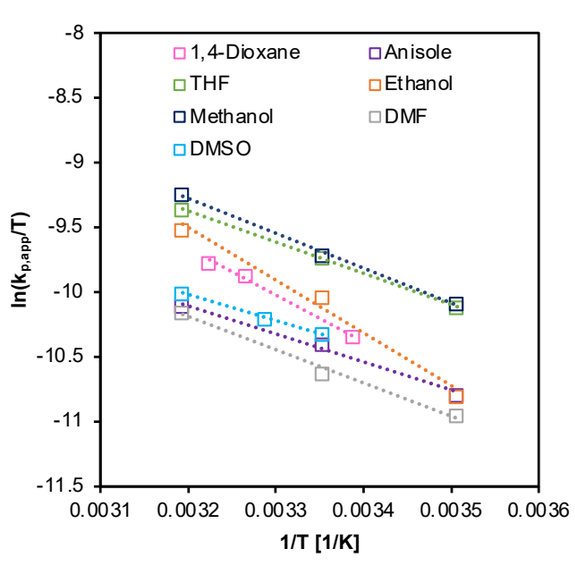


Fig 5. Eyring–Polanyi plot for various solvents. λ_{max} = 450 nm, 18 mW cm^{-2}, 50 %v/v.

Table 1. Arrhenius parameters, enthalpy of activation ($\Delta H^{\ddagger}$), and entropy of activation ($\Delta S^{\ddagger}$)

Solvent	E_a [kJ/mol]	A [L/(mol·s)]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/(mol·K)]
1,4-Dioxane	31.95	4.33×10³	29.49	-183.54
Anisole	20.64	36.05	18.16	-223.44
THF	22.53	154.56	20.04	-211.36
EtOH	36.56	3.03×10⁴	34.07	-167.46
MeOH	24.73	397.86	22.25	-203.475
DMF	23.64	104.99	21.16	-214.55
DMSO	19.05	21.26	16.51	-228.02

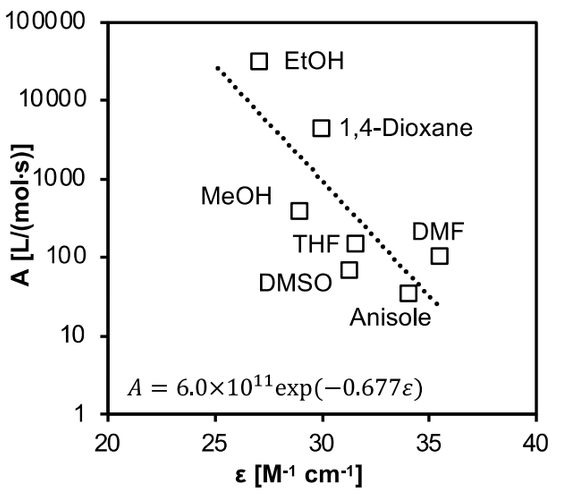


Fig. 6 Pre-exponential factor *A* fitted to an exponential regression model correlated to the extinction coefficients *ε* (r^2 = 0.93).

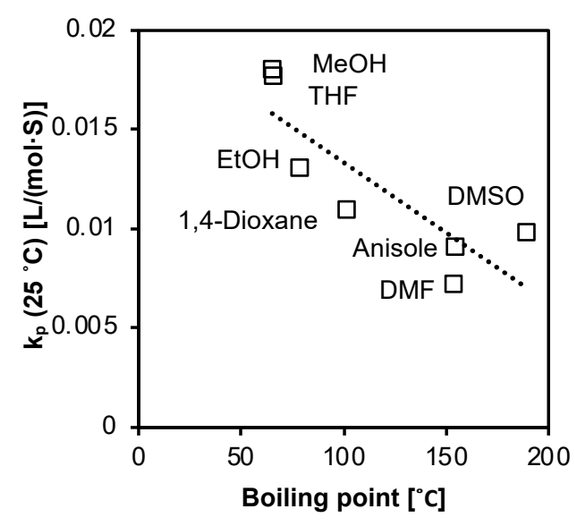


Fig. 7 The values of k_p at 25 °C (r^2 = 0.71) fitted to a linear regression model correlated to boiling points.

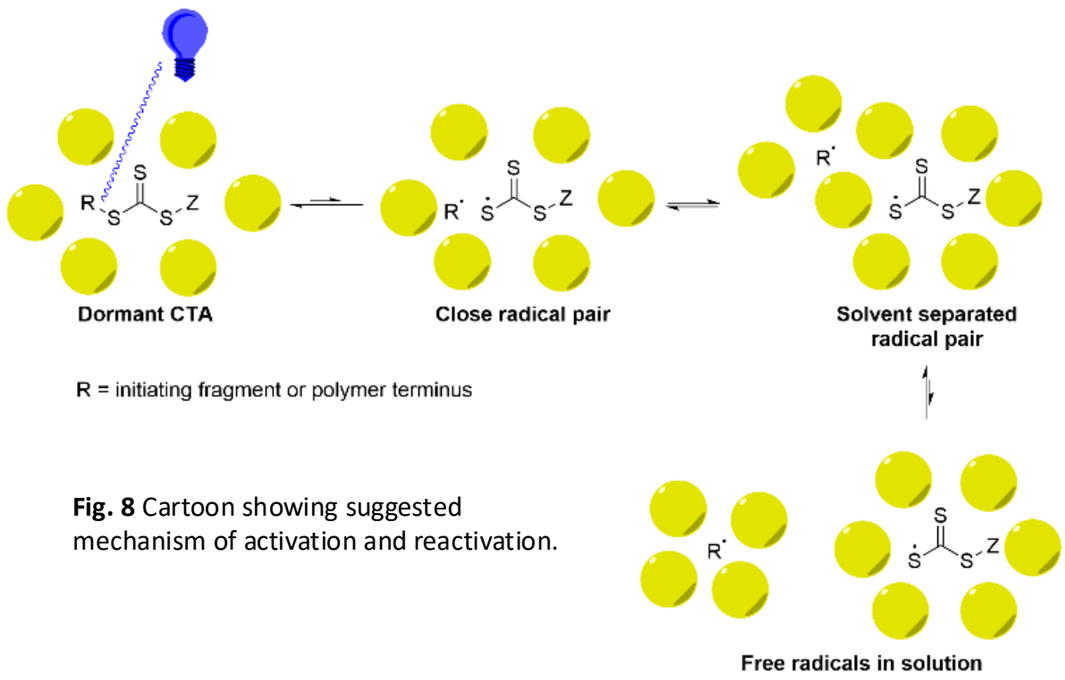


Fig. 8 Cartoon showing suggested mechanism of activation and reactivation.

Conclusions

- The apparent k_p values were affected by equilibria and were sensitive to ambient temperature.
- Arrhenius parameters, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were fitted into Kalmet–Abraham–Taft and Catalan solvatochromic equations. However, no relationship was revealed by the regression analysis.
- The decreasing extinction coefficient of the CTA exponentially increases the effective collision factor A.
- The apparent k_p values have a good relationship with the boiling point. Remodeling of the solvent cage contributes to the escape of propagating species.

References

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[2] M. G. P. Saifer , L. D. Williams , M. A. Sobczyk , S. J. Michaels and M. R. Sherman , *Mol. Immunol.,* **2014**, 57 , 236 —246
[3] A.-C. Lehnen , J. A. M. Kurki and M. Hartlieb , *Polym. Chem.,* **2022**, 13, 1537 -1546

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