

W. Thielemans (PhDCHE) and R. P. Wool

University of Delaware • Center for Composite Materials • Department of Chemical Engineering

## OBJECTIVE

To obtain a mechanistic model describing free radical polymerization behavior accurately, and for which the parameters can be linked to individual processes. The model also has to be simple enough to be fitted by generally available regression fit software and easy enough to be employed without the need for simulations.

Current models:

- *Phenomenological models*: parameters have no physical significance and are just fitted
- *Mechanistic models*: Either too complex for easy application or inaccurate due to oversimplifications

## MECHANISMS

Initiation	$I_2 \longrightarrow 2I^*$	$\frac{d[I_2]}{dt} = -k_d[I_2]$
Inhibition	$R^* + Z \longrightarrow S^*$	$\frac{d[Z]}{dt} = -k_z[Z][R^*]$
Propagation	$R_n^* + M \longrightarrow R_{n+1}^*$	$\frac{d[M]}{dt} = -k_p[M][R^*]$
Termination	$R_1^* + R_2^* \longrightarrow T$	$\frac{d[T]}{dt} = k_t[R^*]^2$

## ASSUMPTIONS

- Perfect inhibition
- Negligible termination
- Monomer-radical reaction independent of monomer species

## MODEL

Coupling of kinetic and diffusion controlled regime

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{kinetic} \exp\left(-k \frac{\alpha}{\alpha_n - \alpha}\right) + \left(\frac{d\alpha}{dt}\right)_{diffusion} \left(1 - \exp\left(-k \frac{\alpha}{\alpha_n - \alpha}\right)\right)$$

Overall model

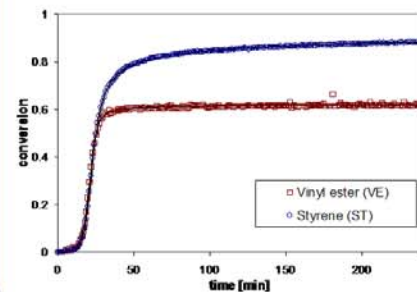
$$\frac{d\alpha}{dt} = K_{p,0}(1-\alpha) \left(1 - \exp(-k_d(t-t_r))\right) \left( (1+m\alpha) \exp\left(-k \frac{\alpha}{\alpha_n - \alpha}\right) + \left(1 - \frac{\alpha}{\alpha_n}\right) \left(1 - \exp\left(-k \frac{\alpha}{\alpha_n - \alpha}\right)\right) \right)$$

- m measurement of thermodynamic interactions
- n measurement of diffusion limitation
- $t_r$  delay due to perfect inhibition
- $\alpha_0$  final conversion
- $K_{p,0}$  propagation rate constant (includes initiator conc.)
- $k_d$  initiator decomposition rate

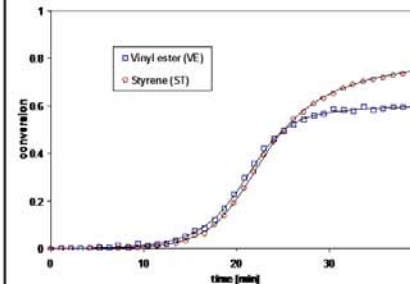
## MATERIALS AND EXPERIMENTS

- Dow Derakane 411-C50  
Vinyl ester + 40wt% styrene
- 2 Initiators  
USP-90MD  
Esperox 28
- Conversion followed by FTIR spectroscopy

## MODEL FIT (1wt% USP-90MD)



## MODEL FIT (1wt% USP-90MD)



## CONCLUSIONS

- Simple model was obtained (regression can be done by generally available software, e.g. Sigmaplot)
- Parameters m, n, k,  $\alpha_0$ , independent of initiator
- Values for m, n and k can be explained and predicted from physical processes,
- $k_d$  obtained from initiator half life data can be used

## ACKNOWLEDGEMENTS

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