

# Influence of hydroxyl concentration on the cure kinetics of DGEBA epoxy in the presence of a tertiary amine

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## Introduction

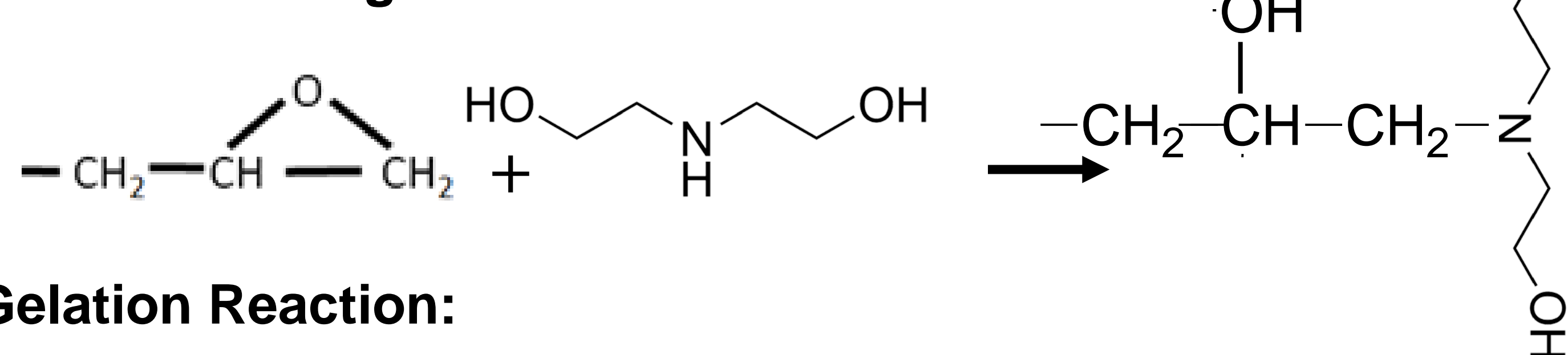
DGEBA is reacted with hardener mixtures of DEA and DBA. Both DEA and DBA have a secondary amine that reacts rapidly with epoxide, forming a non-crosslinked adduct in about 30 minutes under normal, 70°C, cure conditions. The subsequent crosslinking reaction is slower, taking 24 hrs to near completion for DGEBA/DEA.

DGEBA/DEA/DBA mixtures keep epoxide/amine mole ratio constant (at 4.8:1) and vary epoxide/hardener-hydroxyl ratio from 2.4:1 for a hardener of pure DEA to 1:0 for pure DBA. Expectations during the cure reaction include: 1) that proton transfer plays a major role at high [OH] (high DEA/DBA ratio); 2) that high [OH] results in a high reaction rate; and 3) that low [OH] (low DEA/DBA ratio) results in a negligible reaction rate. *These expectations are shown to be overly simplistic.* At 70°C the maximum reaction rate occurs at roughly 25% DBA, indicating that there is an optimal [OH] to facilitate reaction kinetics.

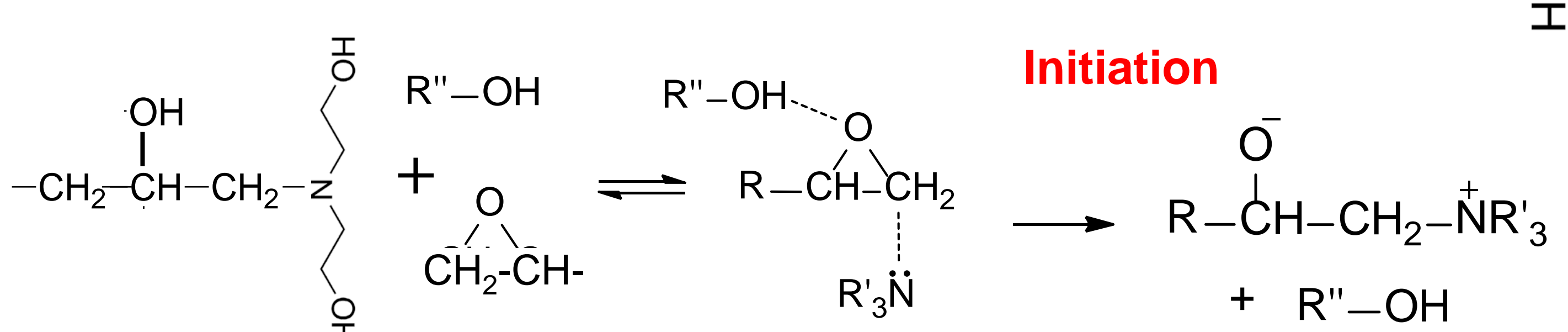
**Experiment:** DGEBA, DEA and DBA are heated to reaction temperature. Wt. mix ratio 100:12 DGEBA:DEA. Amount of DBA to substitute for DEA keeps amine/epoxide ratio fixed. Heat of reaction measured in air cooled Thermal Activity Monitor (TAM air – TA instruments). Temperature ramps and some isotherms in Q2000 DSC (TA instruments).

## Major Reactions

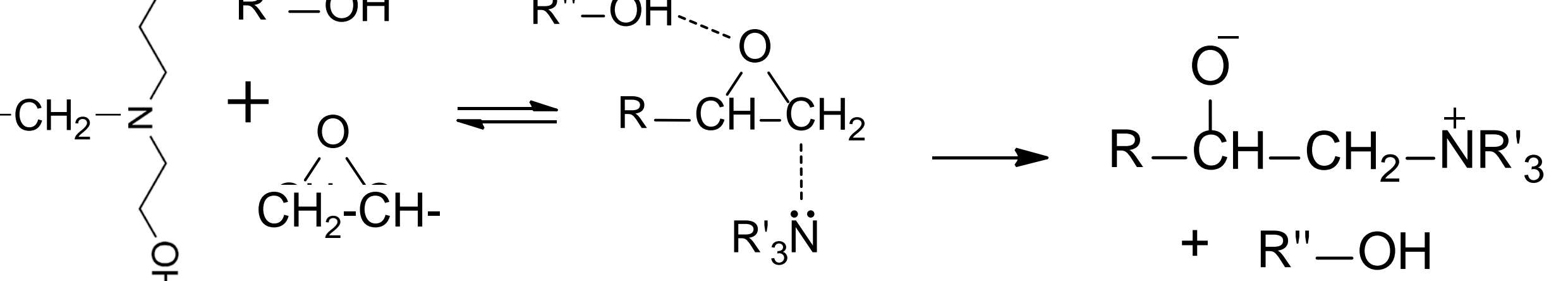
### Adduct Forming Reaction:



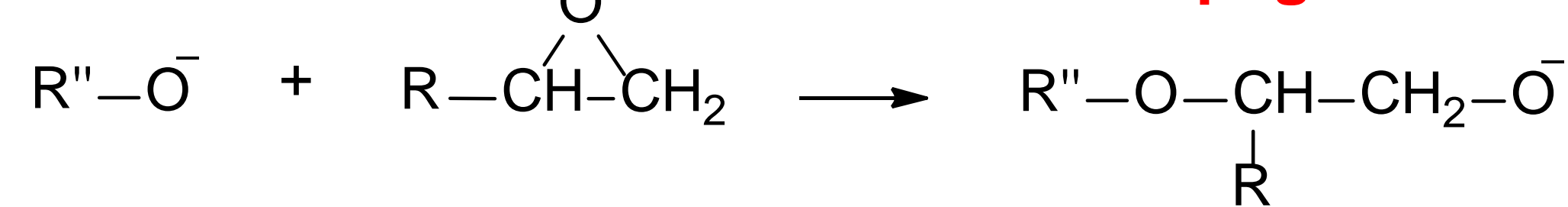
### Gelation Reaction:



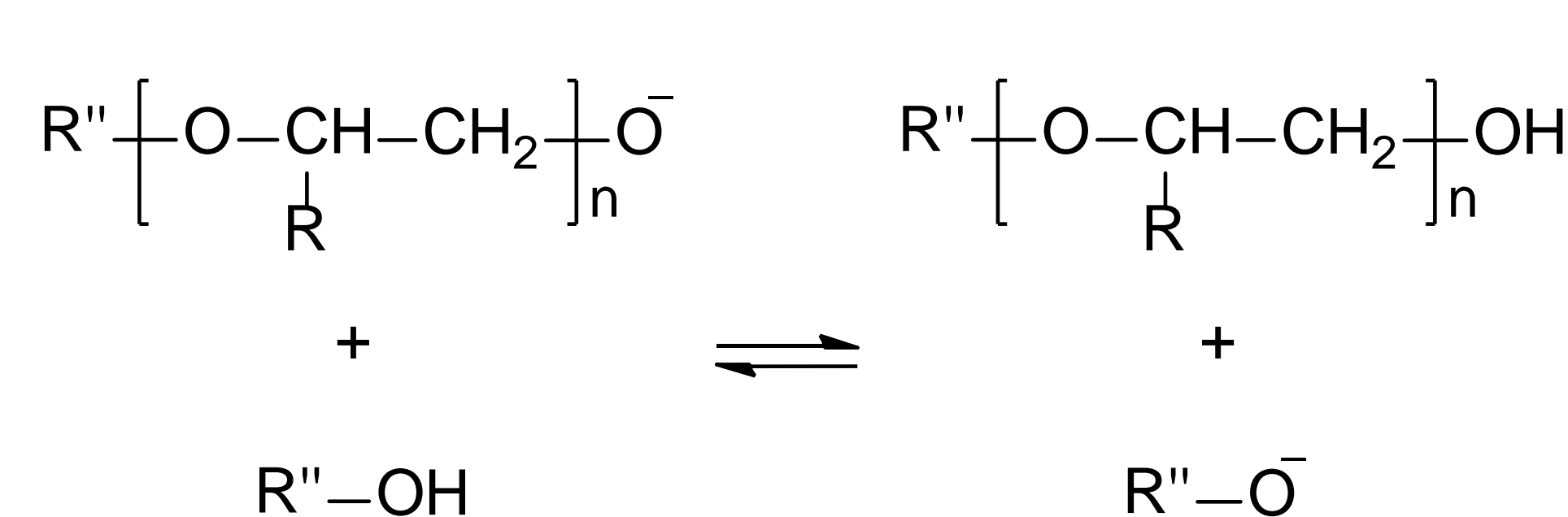
### Initiation



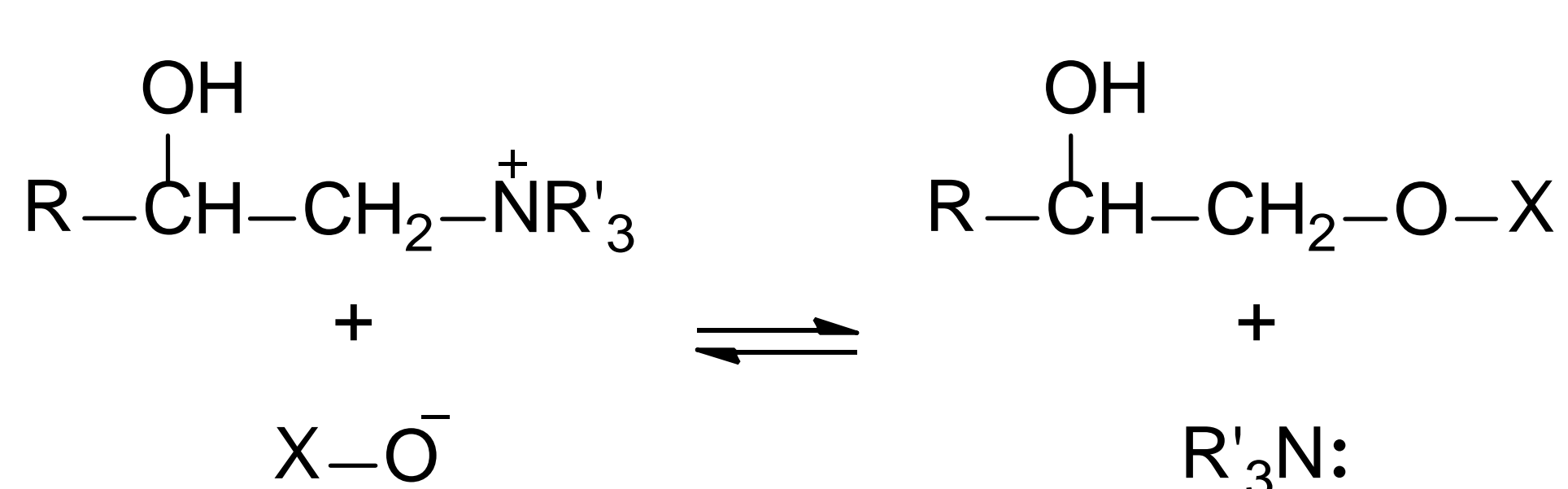
### Propagation



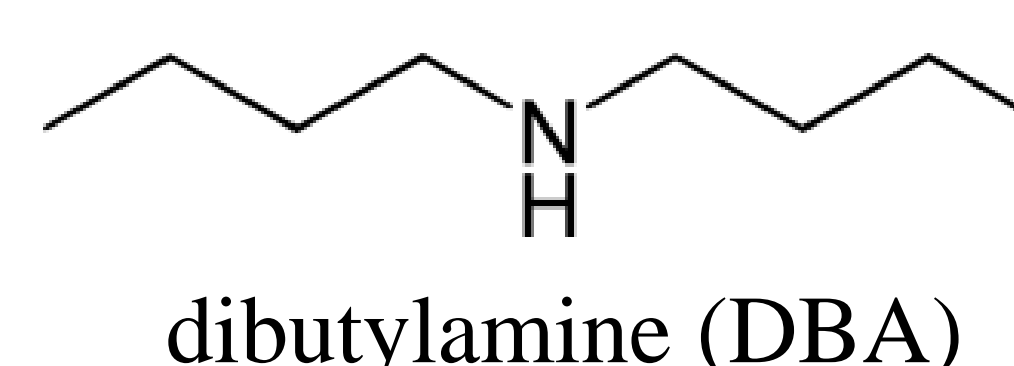
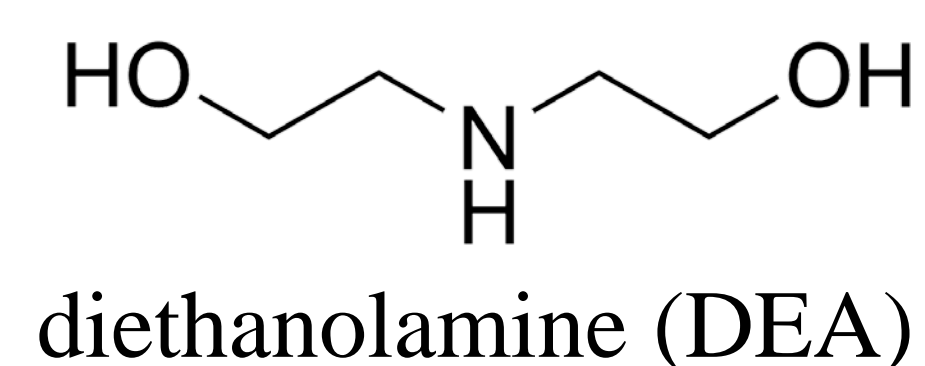
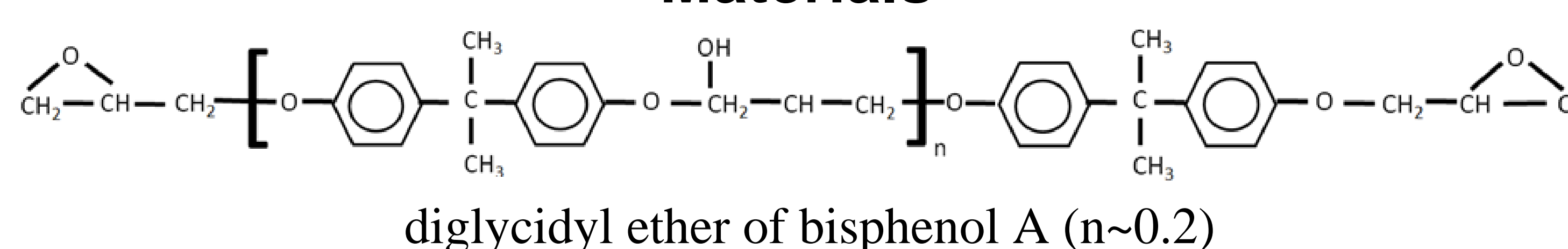
### Proton Transfer



### Termination

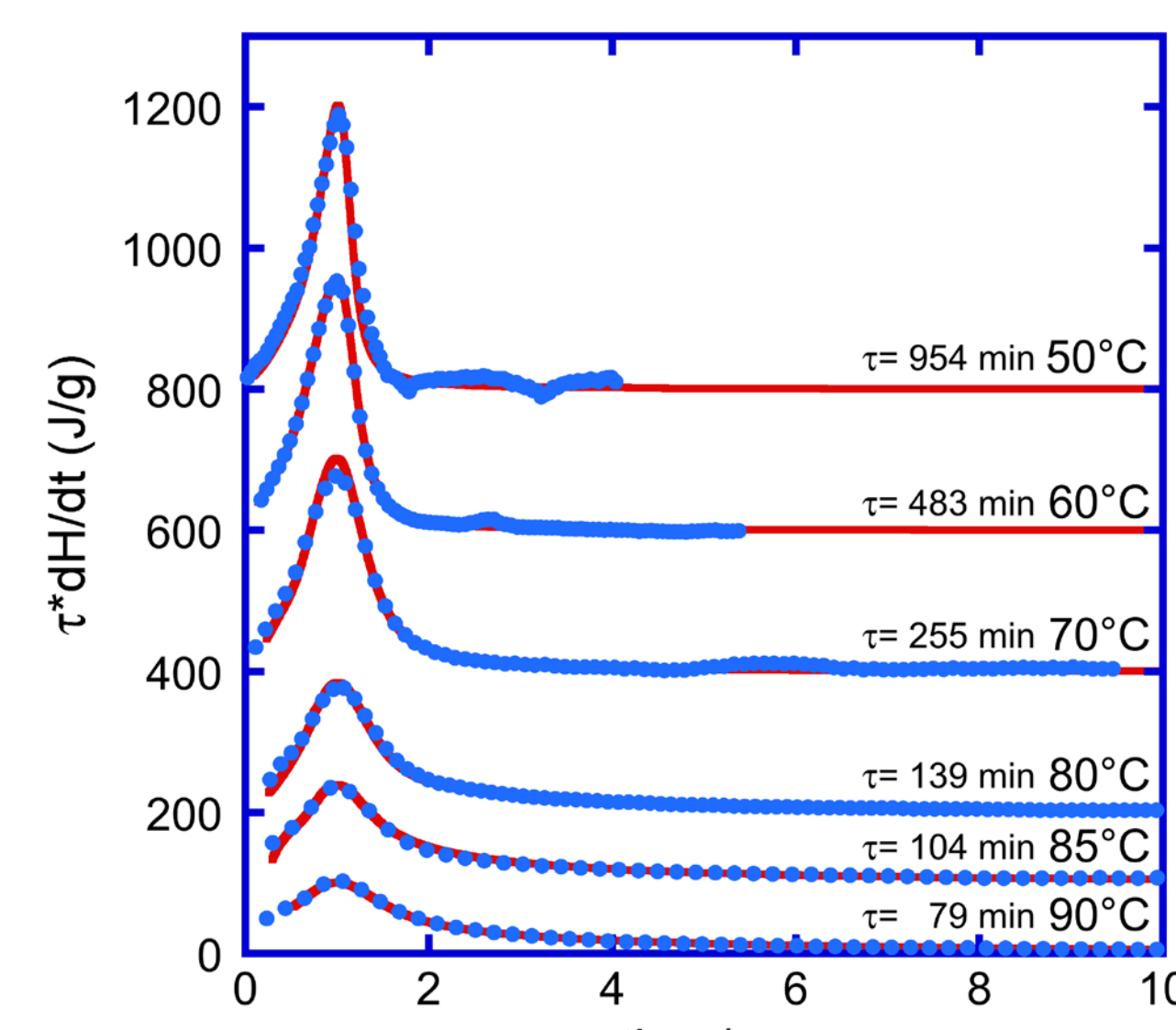


## Materials

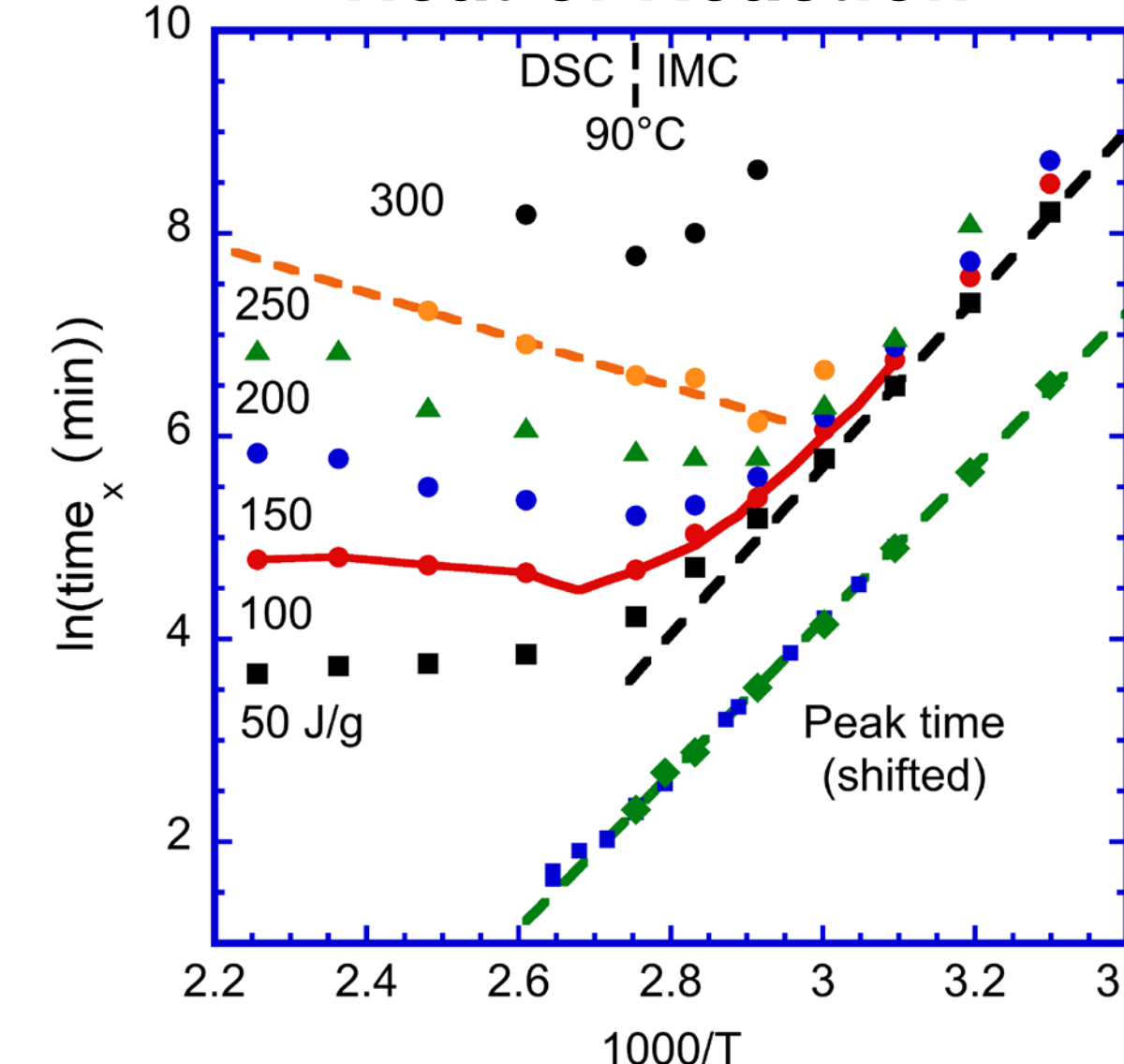


## Reaction of DGEBA and Diethanolamine

### Isothermal Cure

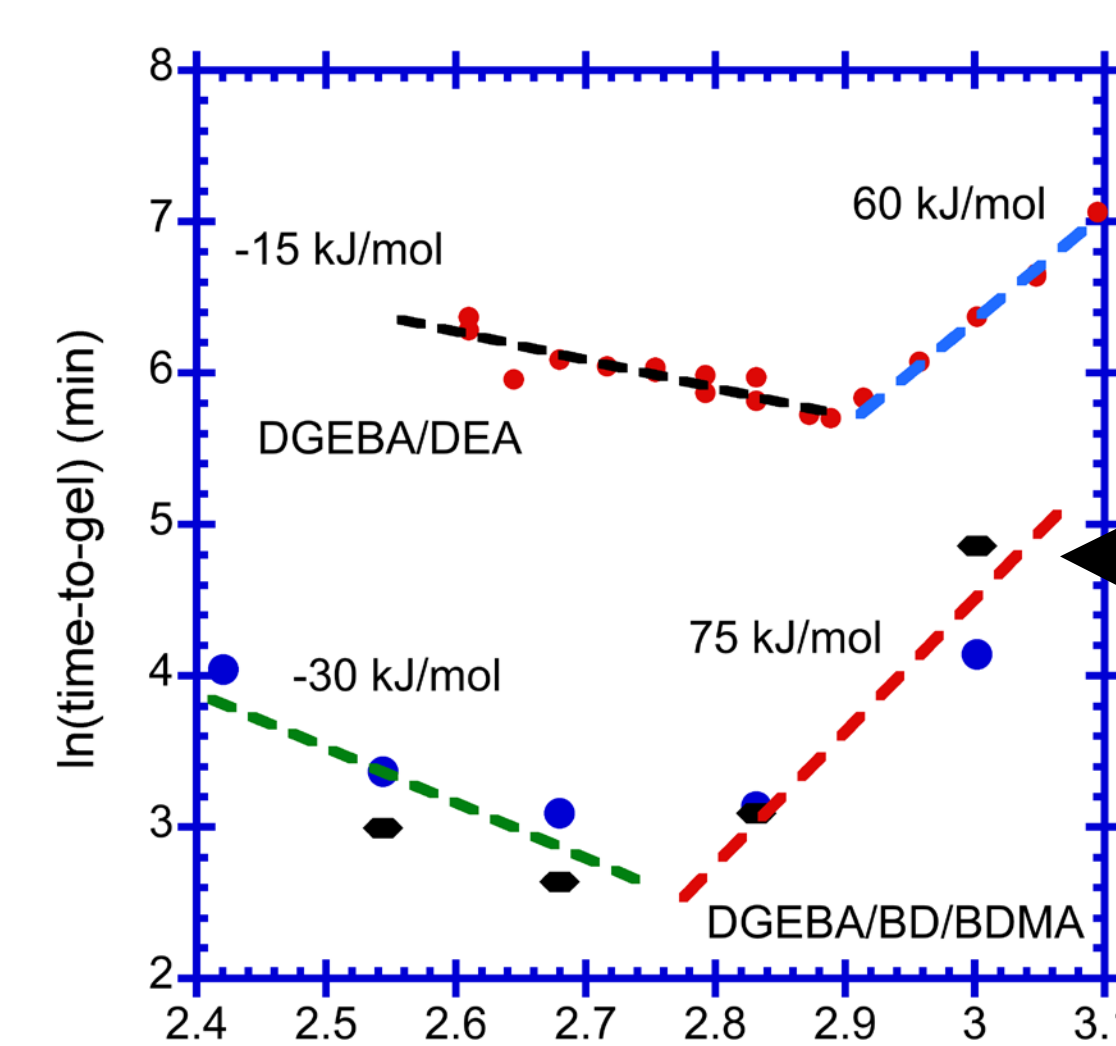
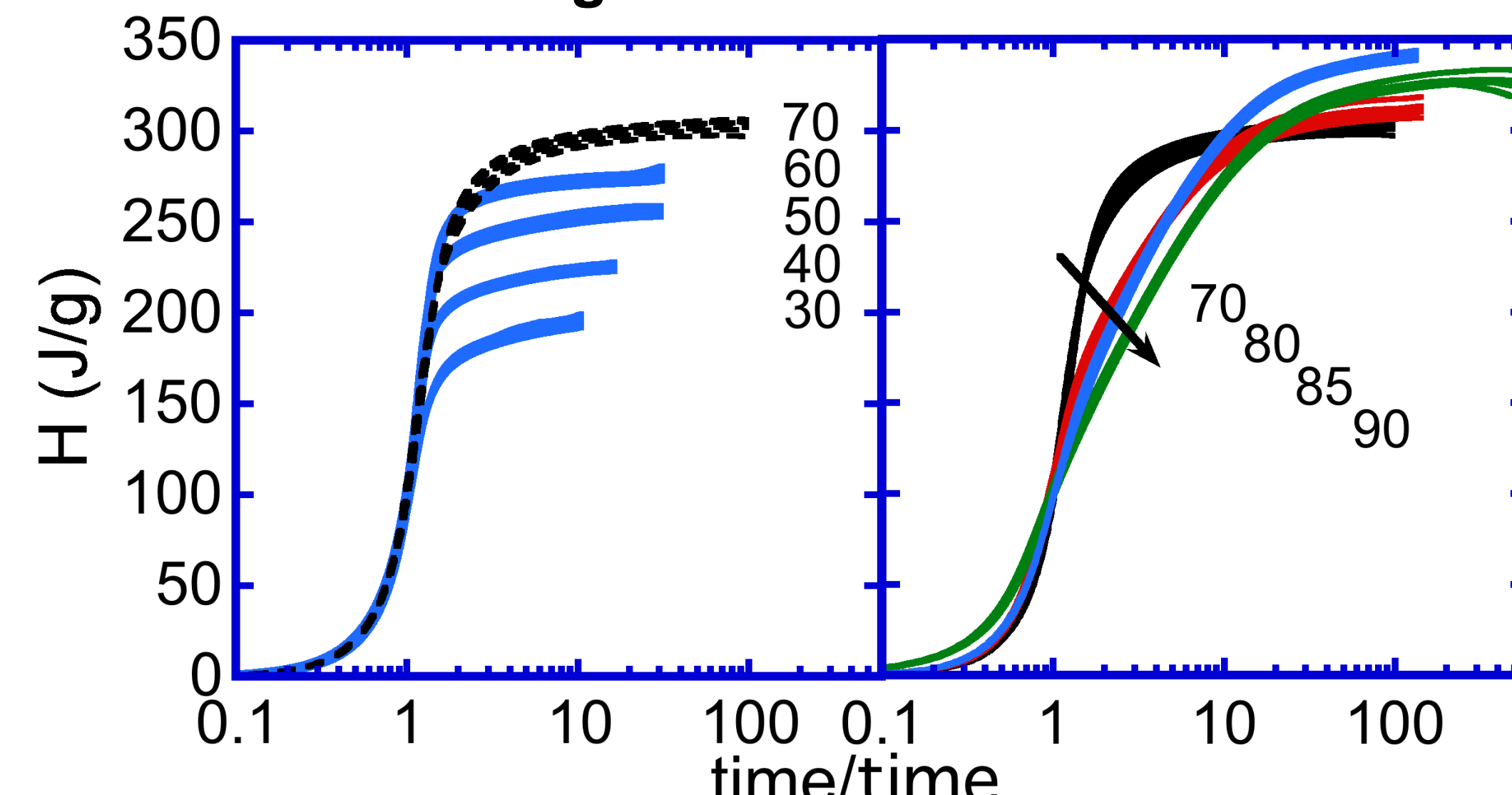


### Time to "x J/g" integrated Heat of Reaction

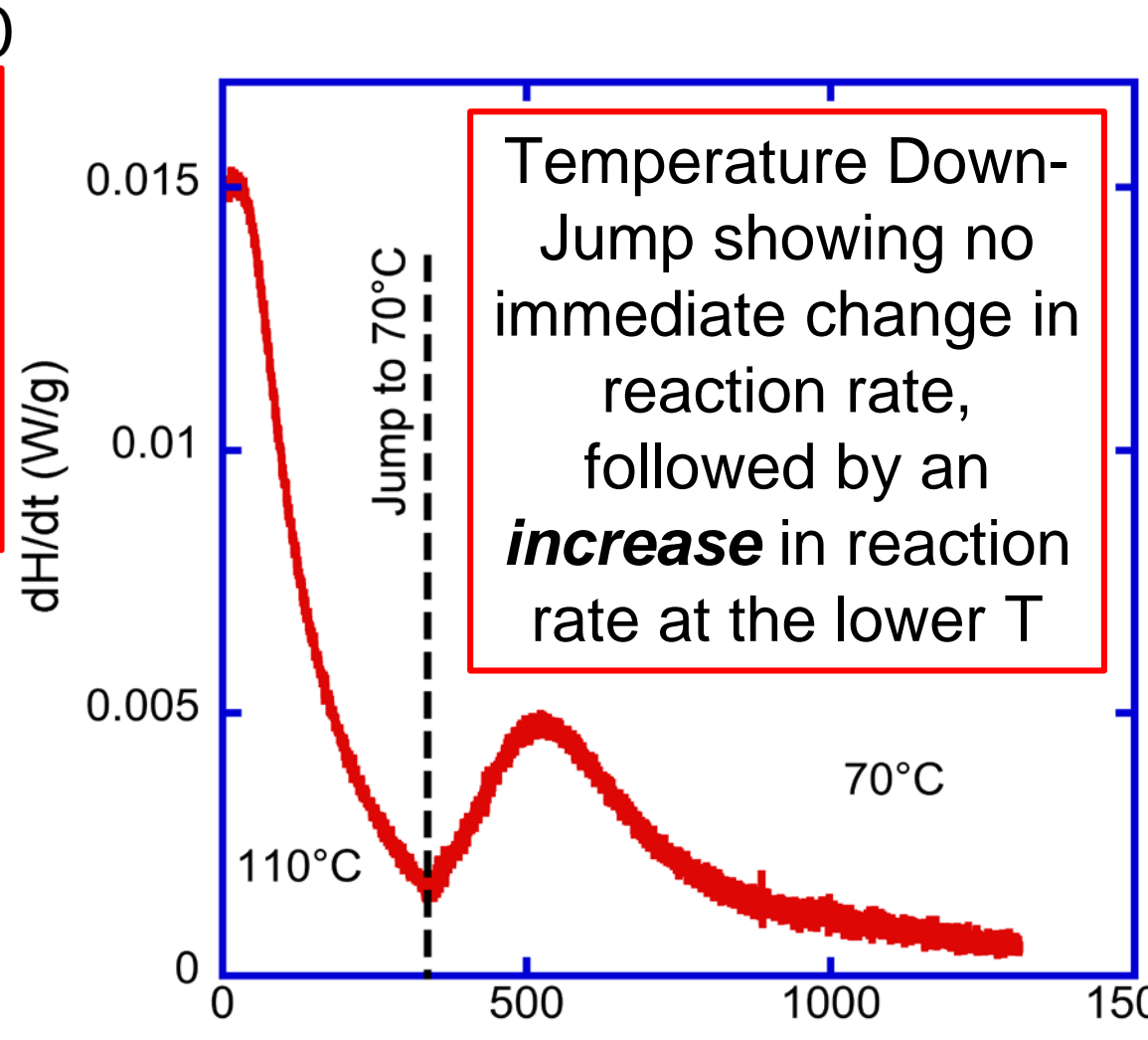


If "Simple" Kinetics, curves would be identical  $\frac{d\alpha}{dt} = K(T)f(\alpha)$

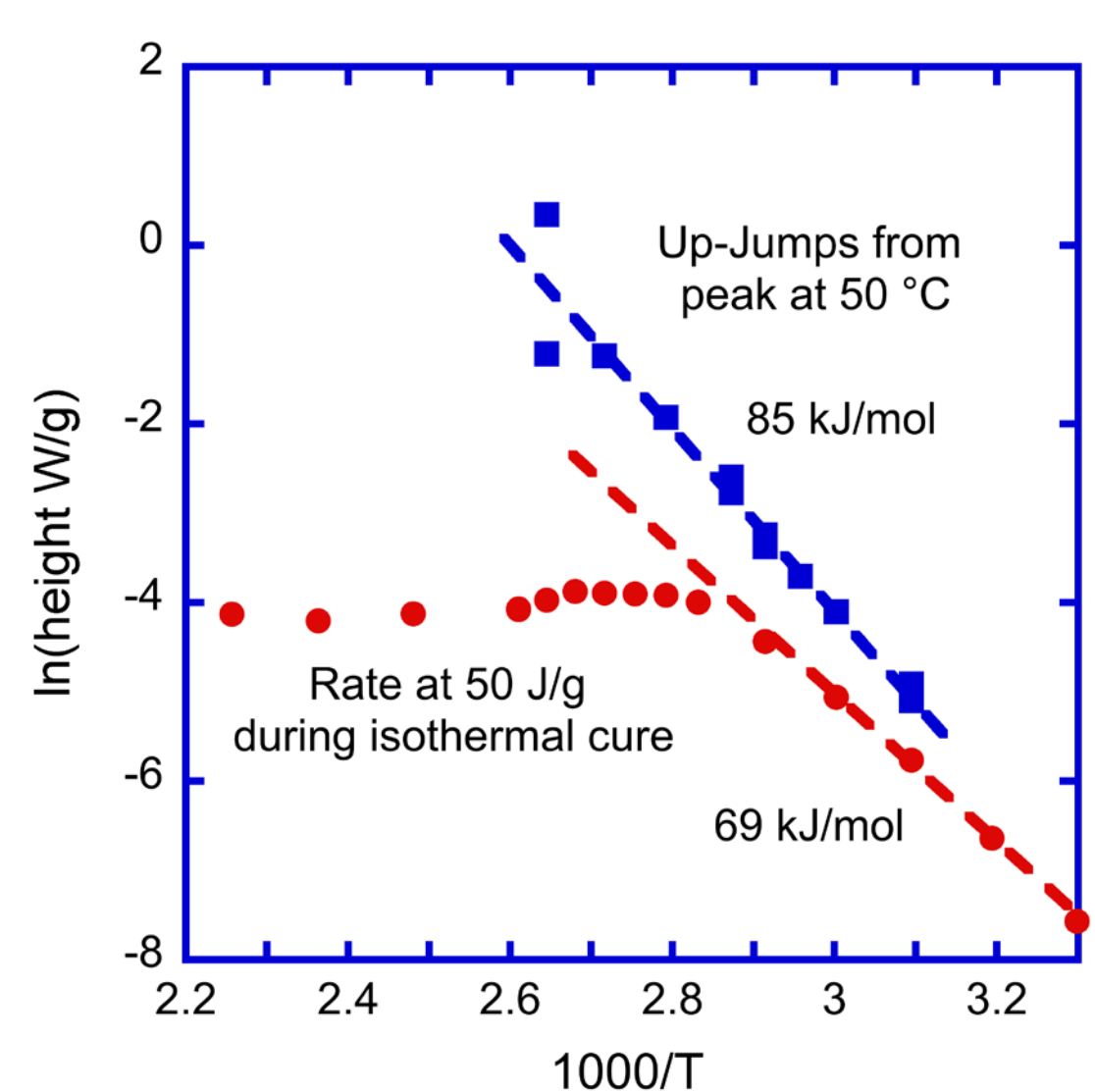
### Integrated Heat of Reaction



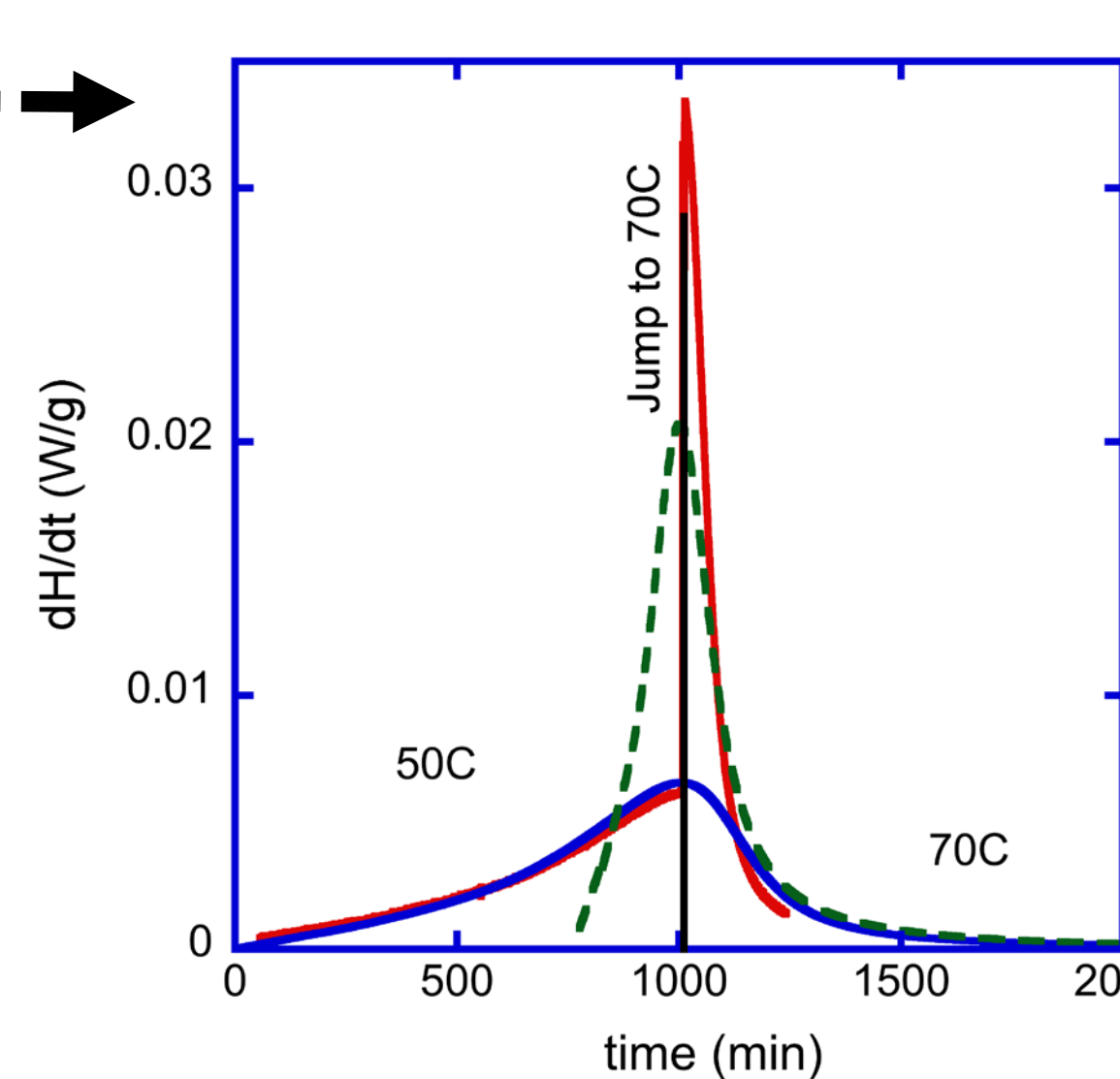
Time to gel shows slowing down of reaction at high T. Comparison to work of Tanzer [3] for DGEBA, benzyl dimethylamine (BDMA) and butanediol (BD)



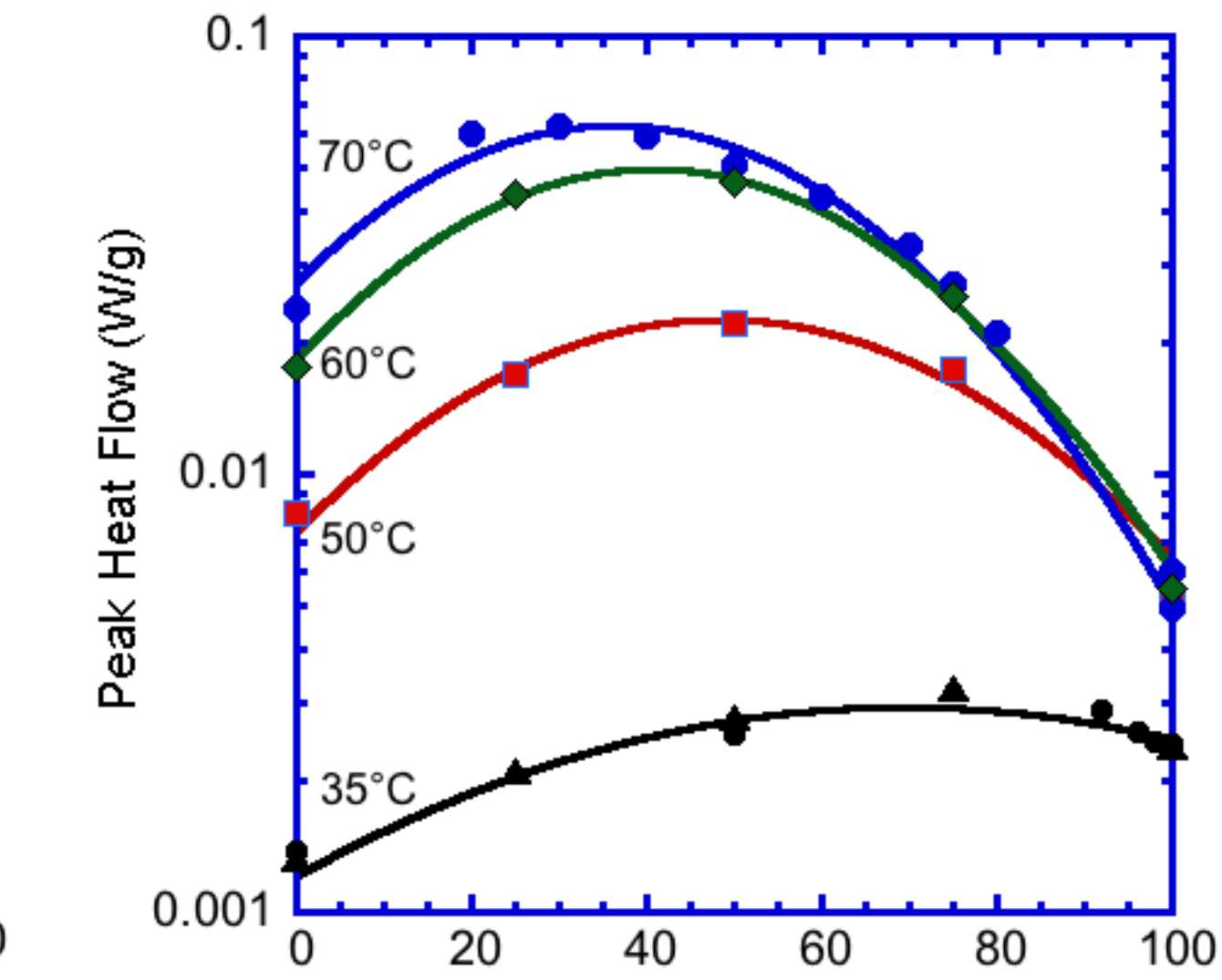
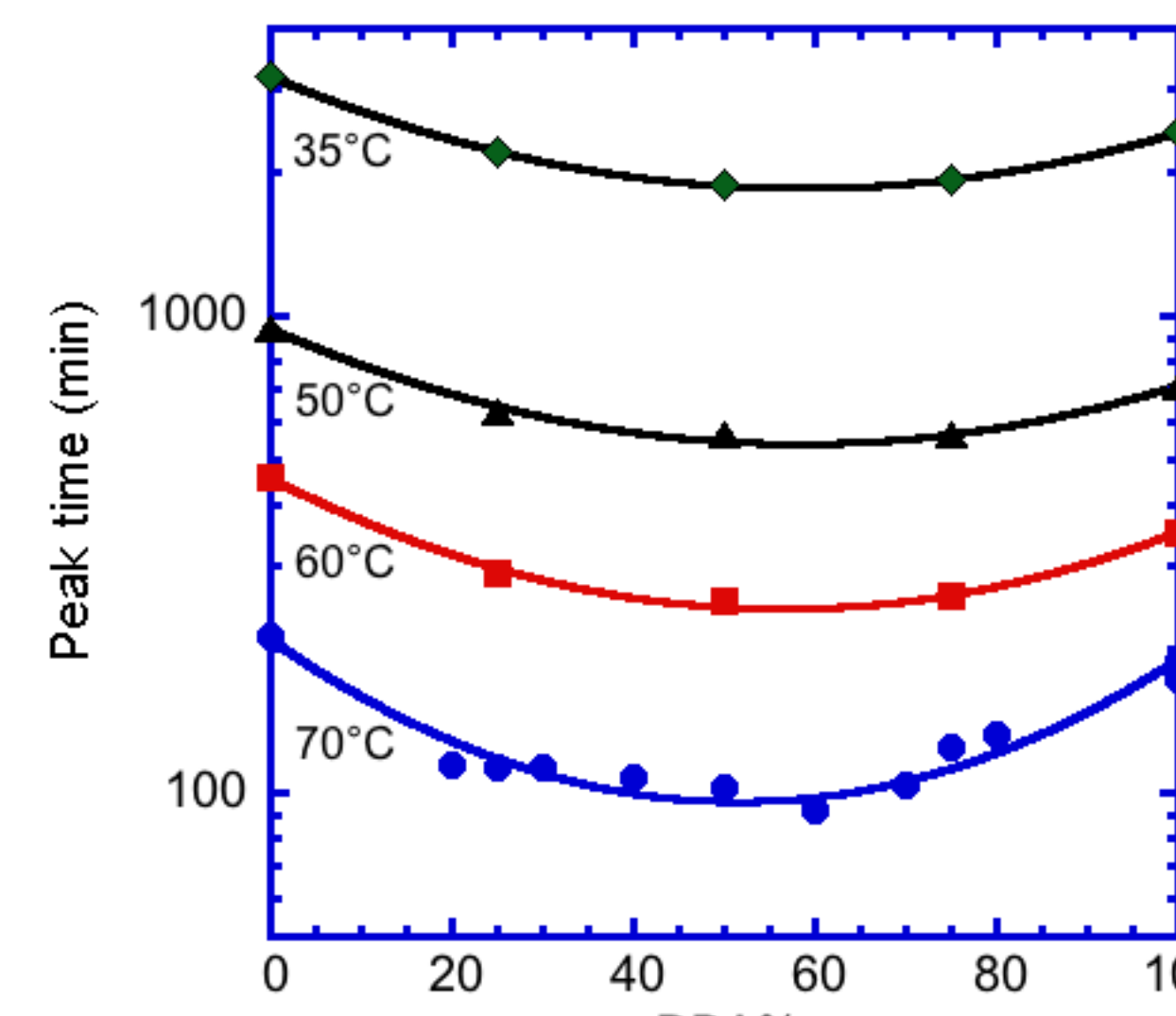
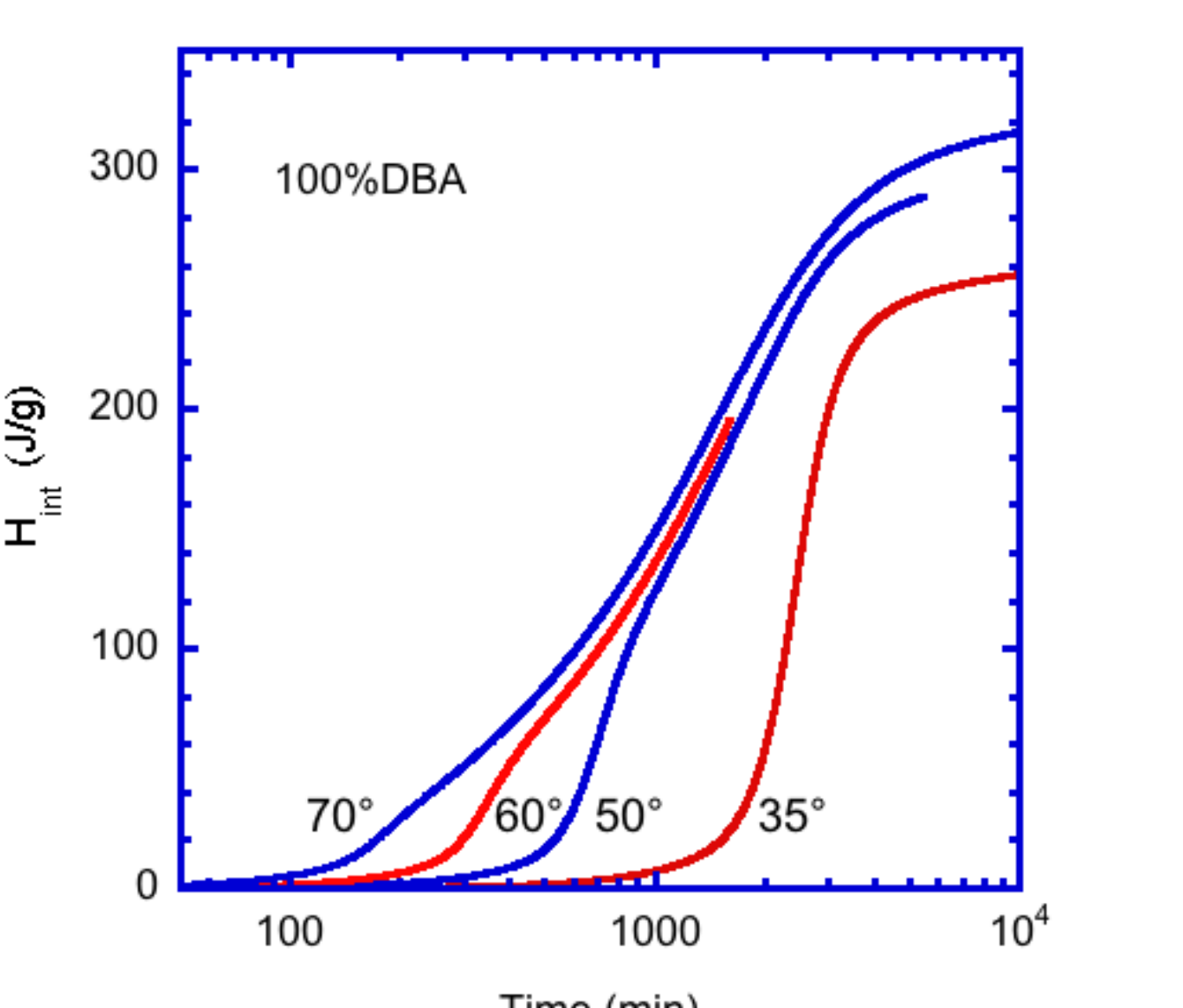
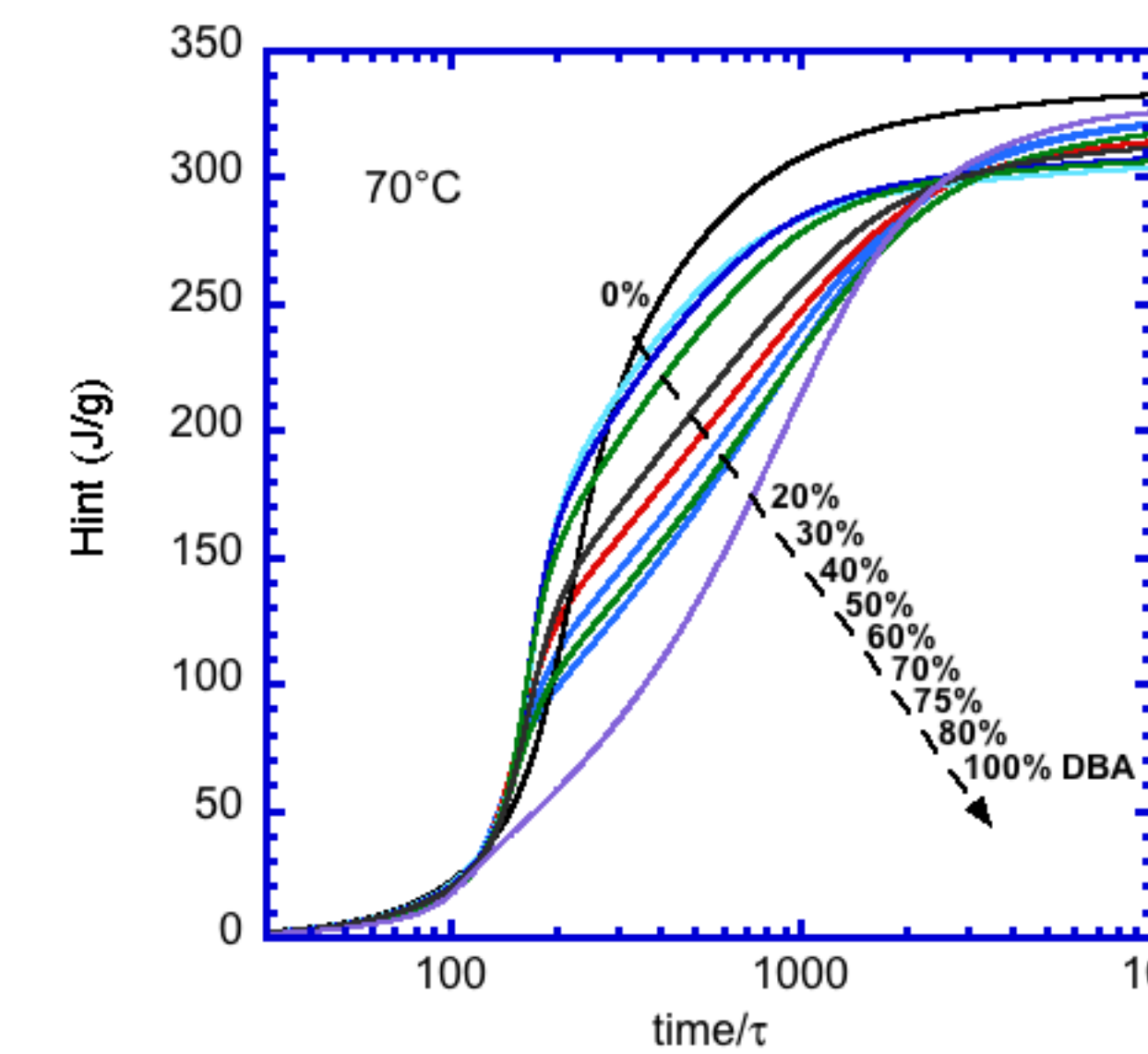
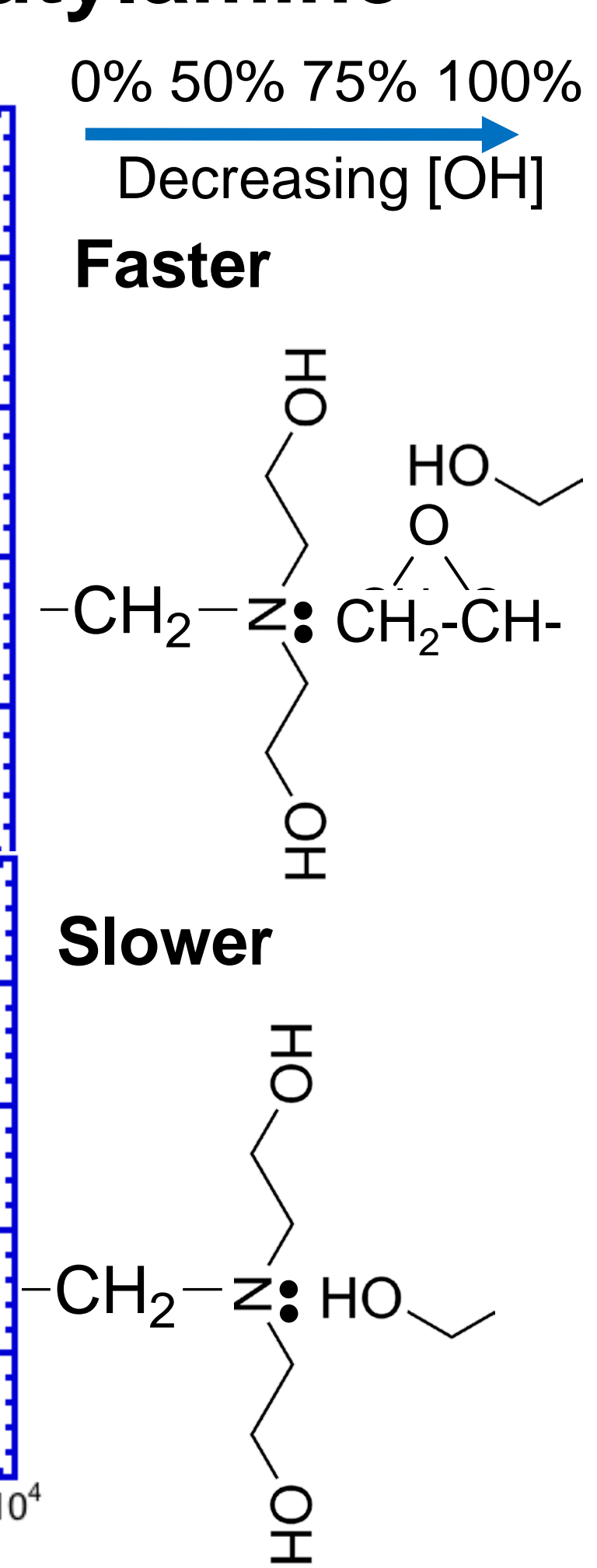
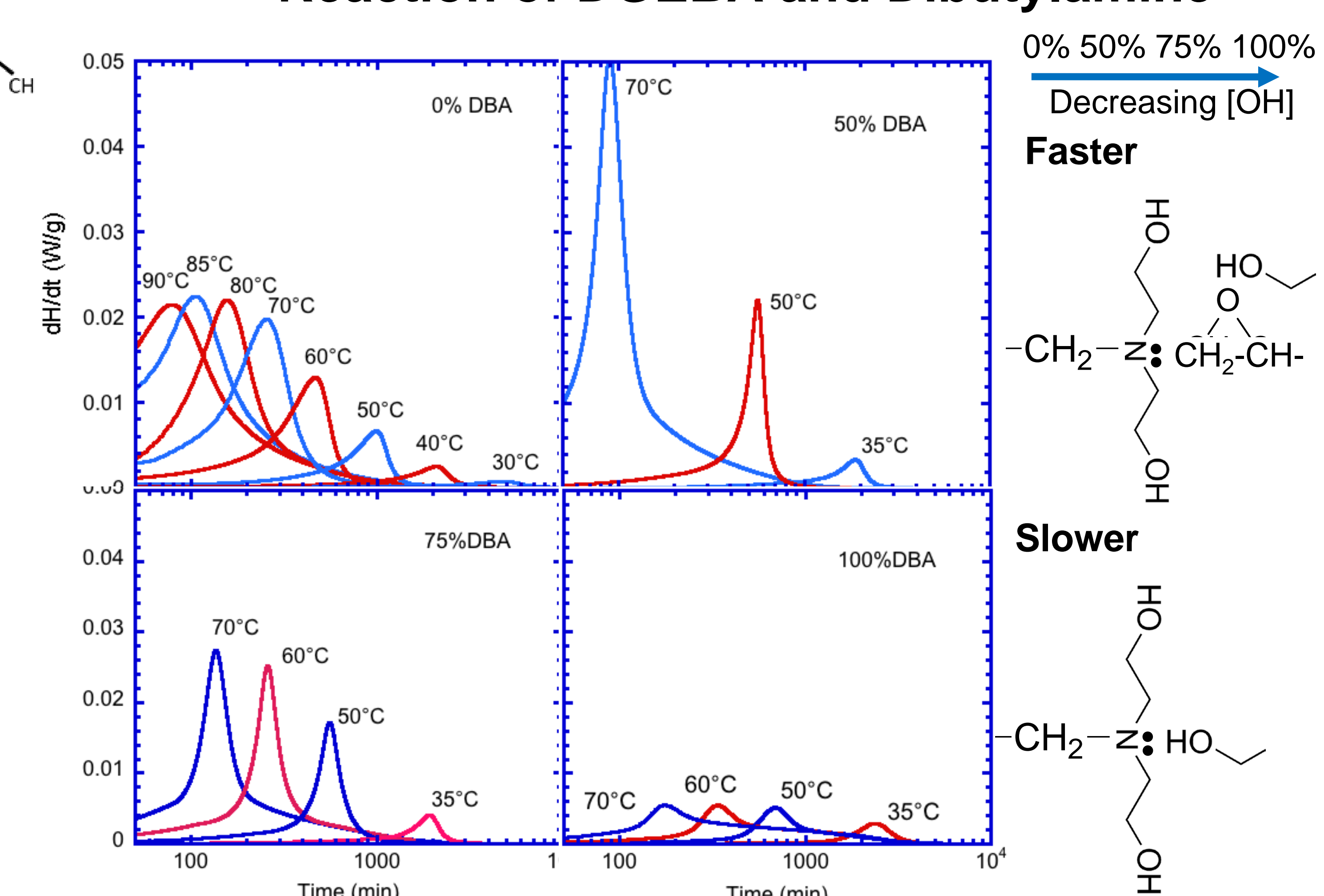
Temperature Down-Jump showing no immediate change in reaction rate, followed by an **increase** in reaction rate at the lower T



Temperature Up-Jump showing reaction rate after the jump to be higher than any rate observed when cured at higher T. Implies  $E_a$  of propagation reaction ~85kJ/mol (as compared to  $E_a$  of ~69kJ/mol from peak time of total reaction). Further evidence that anionic concentration is function of T.



## Reaction of DGEBA and Dibutylamine



## Conclusions:

- DGEBA/DEA has ceiling temperature above which reaction slows.
- Decreasing [OH] at first accelerates and then decelerates reaction.
- Increasing DBA similar to effect of increasing temperature on DGEBA/DEA. -change of shape of Hint vs. time.
- Up and down jumps better isolates temperature effects - implies decrease of initiator with increasing T.

## References

[1] J.D. McCoy, W.B. Ancipink, C.M. Clarkson, J.M. Kropka, M.C. Celina, N.H. Giron, L. Hailasilassie, N. Fredj, *Cure mechanisms of diglycidyl ether of bisphenol A (DGEBA) epoxy with diethanolamine*, Polymer 105 (2016) 243-254  
 [2] J.D. McCoy, W.B. Ancipink, S.R. Maestas, L.R. Draelos, D.B. Devries, J.M. Kropka, *Reactions of diglycidyl ether of bisphenol A (DGEBA) epoxy cured with diethanolamine: Unusual dependencies on temperature and extent of reaction and implications to network structure*, Submitted (2018)  
 [3] W. Tanzer, S. Reinhardt, M. Fedtke, *Reaction of glycidyl ethers with aliphatic-alcohols in the presence of benzyl dimethylamine*, Polymer 34(16) (1993) 3520-3525.