Polymerization of γ-Benzyl-L-glutamate-N-carboxyanhydride (GluNCA) Kinetics Study

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Goal

Kinetic Study

To determine the rate of the polymerization

Method

Measure the concentration of the monomer using IR Spectrometry to determine the rate of reaction

Polymerization using Monofunctional and Difunctional Initiators

<u>Monofunctional</u>

$I + M \rightarrow IM^*$

$IM^* + M \rightarrow IMM^*$

$IMM^* + M \rightarrow IMMM^*\ldots$

<u>Difunctional</u>

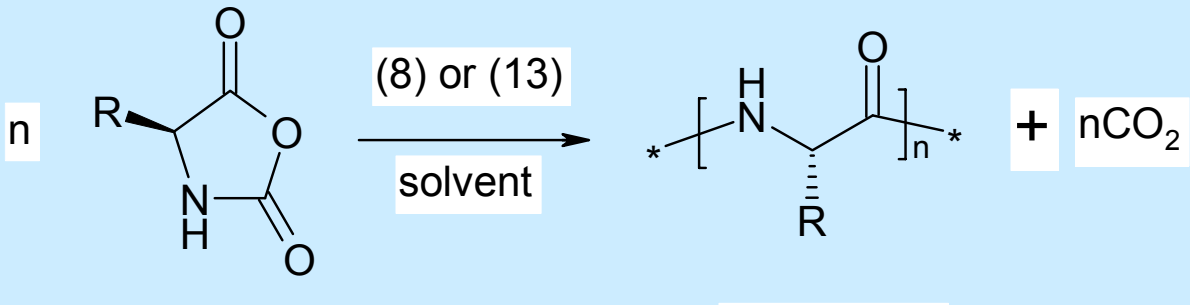
$I + M \rightarrow {}^*MIM^*$

${}^*MIM^* + M \rightarrow {}^*MMIMM^*$

${}^*MMIMM^* + M \rightarrow \ldots {}^*MMM\ IMMM^*\ldots$

I= initiator
M=monomer
*= active site at which additional monomers are added

Polymerization of GluNCA

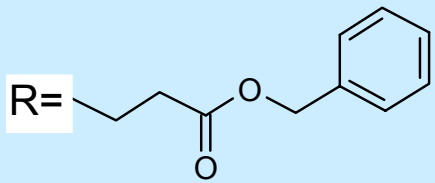


GluNCA

(γ-benzyl Glutamate NCA)

Polypeptide

Repeat unit

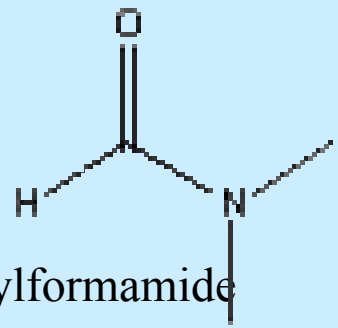


Solvent:

THF

Tetrahydrofuran

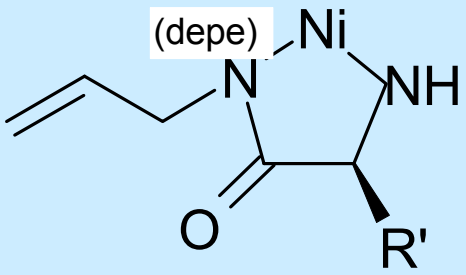
DMF



N,N'-Dimethylformamide

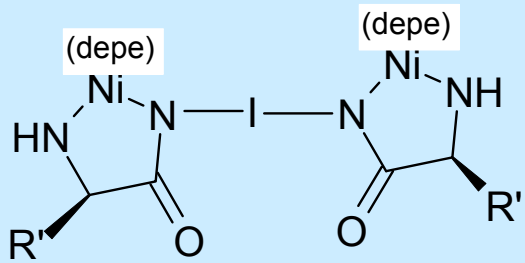
Initiators

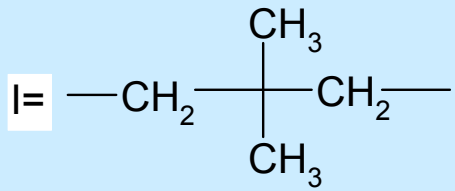
(13)



Monofunctional

(8)



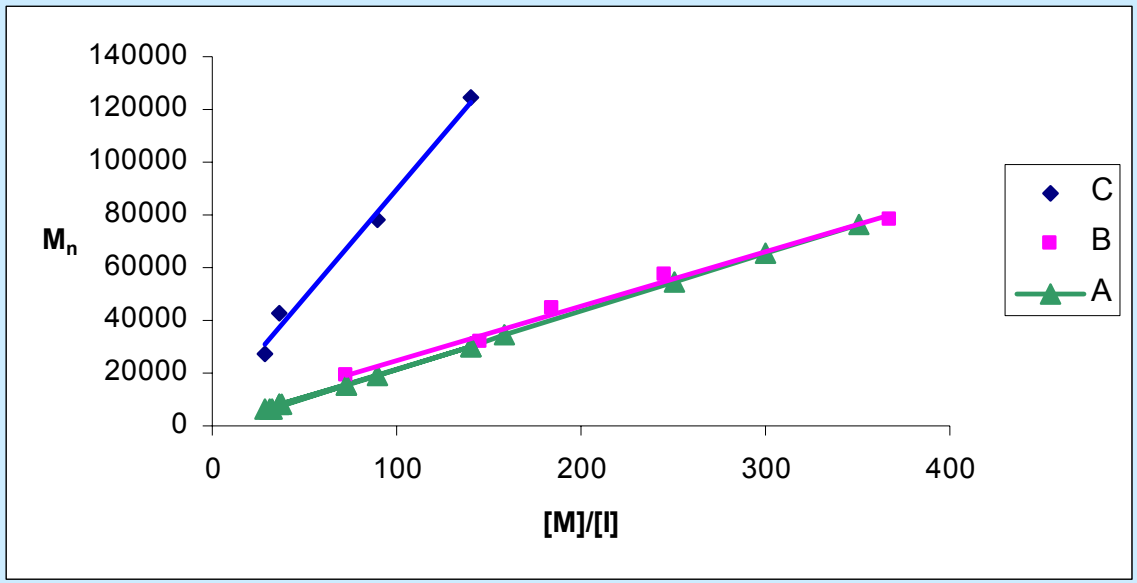


Difunctional?

Depe=1,2-bis(diethylposhino)ethane

R'= $-CH_2CH_2(CH_3)_2$

Molecular Weights of Polypeptides vs. [M]/[I]



M_n= [M]/[I] x M_n (repeat unit)

A= Theoretical M_n
B= (8) in DMF
C= (8) in THF

M_n(DMF) ~ M_n(Theory) "Living Polymerization"

M_n(THF) ~ 5 M_n(Theory)

Determining Rate Constants (k)

$$-\ln(M_t/M_o)=k_{obs}\,t$$

M_t= concentration of monomer at time (t)

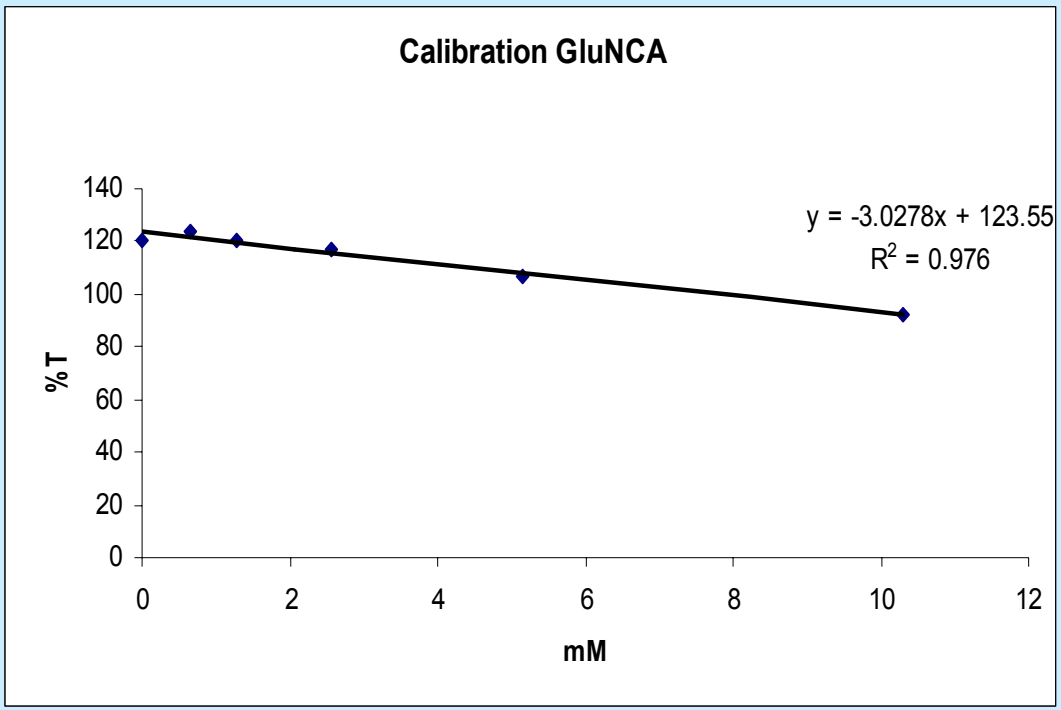
M_o=initial concentration of monomer

k_{obs}=rate constant

t=time

Calibration

- Used to measure monomer (GluNCA) concentration during the reaction
- Signal for carbonyl group measured by IR at 1784.8cm^{-1}



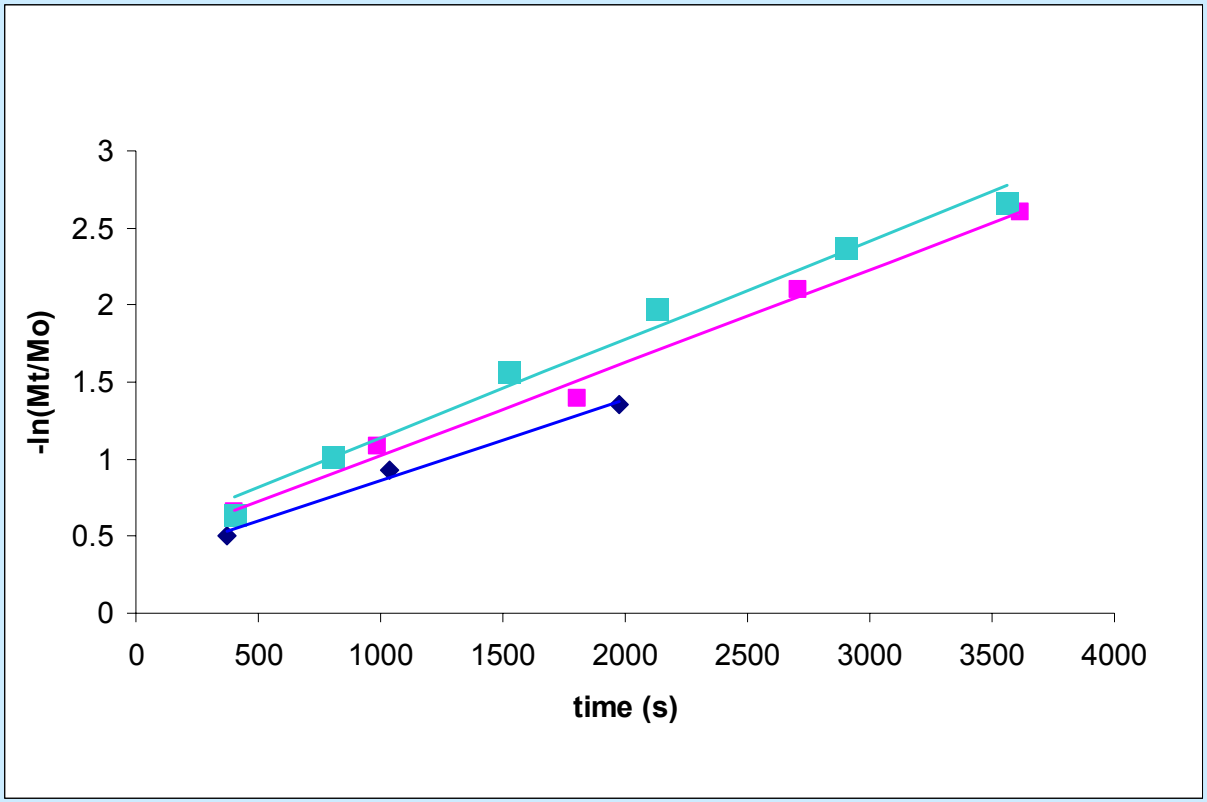
$y = -3.0278x + 123.55$

y= %T

x=concentration of monomer after time $[M]_t$

$$X = \frac{\%T - 123.55}{-3.0287}$$

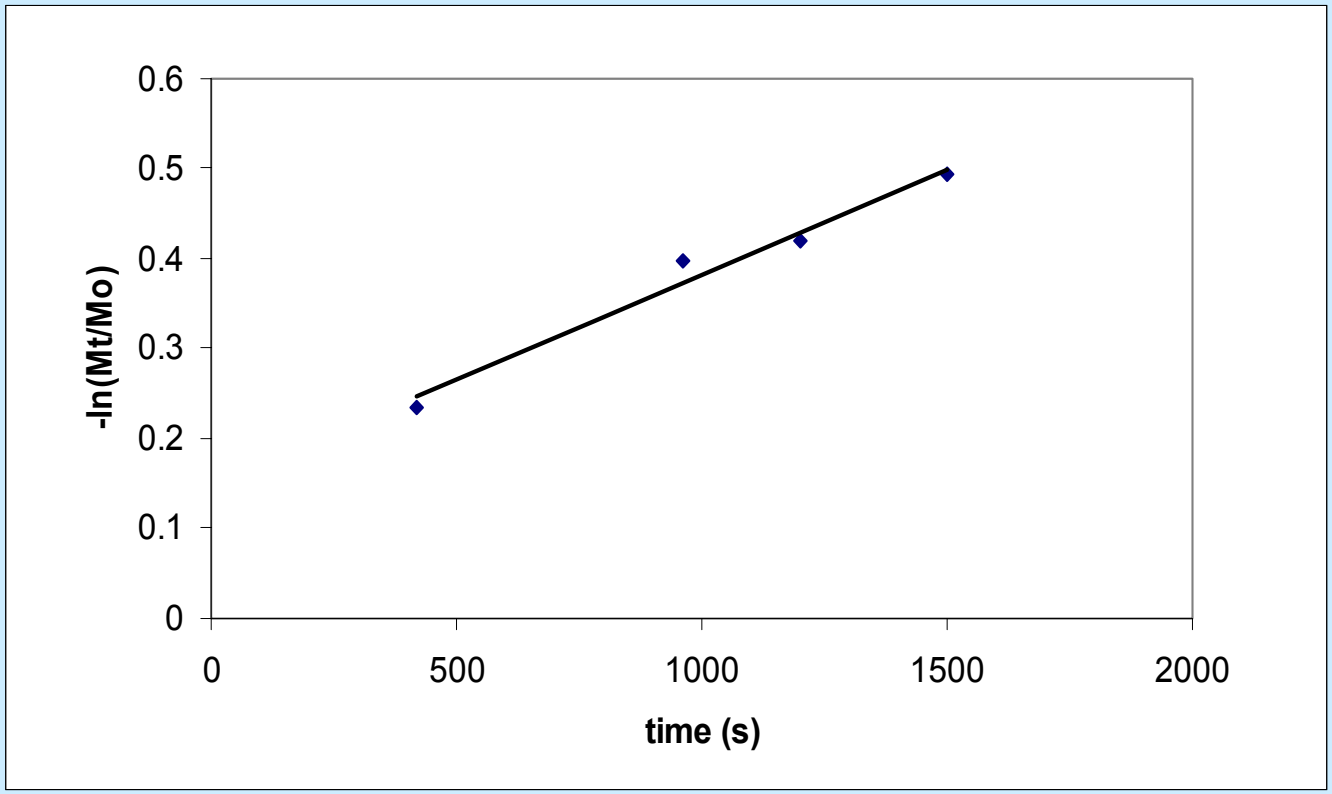
Kinetics for (8) in THF



$[M]_o$=0.13M
$[Init]_o$=1.2x10^{-3}M

k_{obs}= (5.7±0.5)x$10^{-4}$$sec^{-1}$

Kinetics for (13) in THF



$[M]_o$=0.13M
$[Init]_o$=1.2x10^{-3}M

$k_{obs}(13)$=2x$10^{-4}s^{-1}$

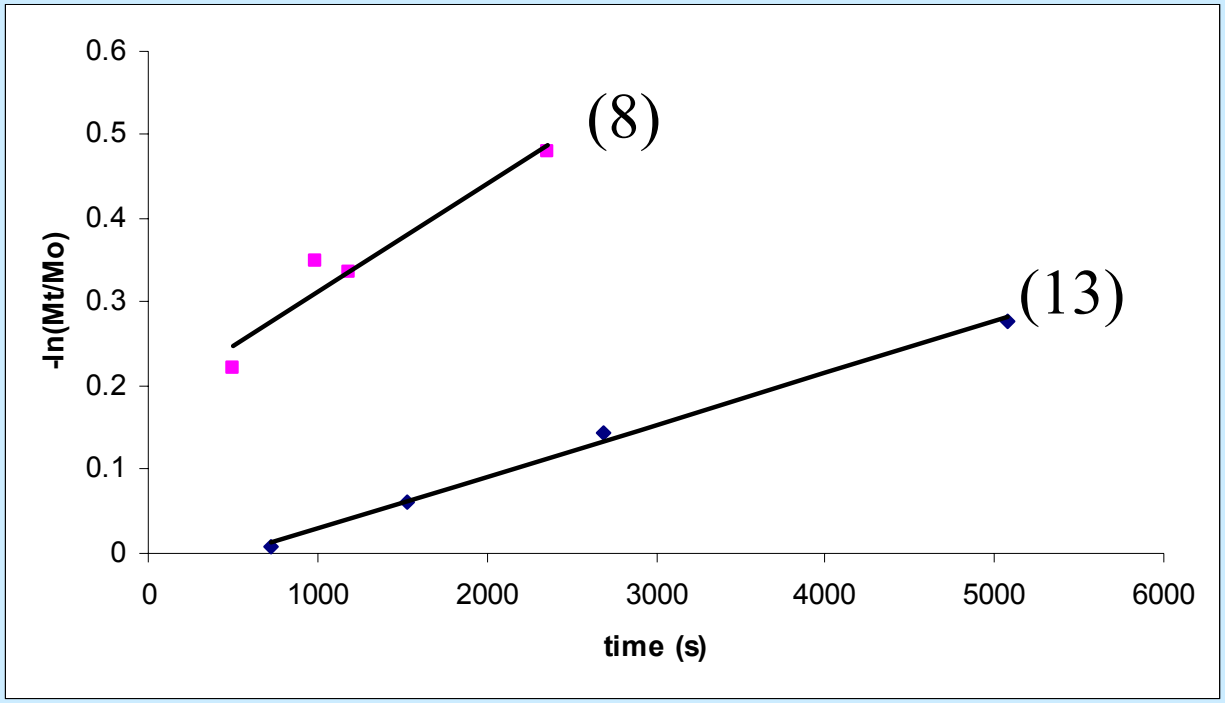
Kinetics for (13) and (8) in THF

$k_{obs}(13)=2x10^{-4}s^{-1}$

$k_{obs}(8)= (5.7\pm0.5)x10^{-4}sec^{-1}$

$k_{obs}(8)> k_{obs}(13)$

Kinetics for (13) and (8) in DMF



$[M]_o$=0.13M
$[Init]_o$=1.2x10^{-3}M

$k_{obs}(13)$=6x$10^{-5}s^{-1}$
$k_{obs}(8)$=1x$10^{-4}s^{-1}$

$_{obs}(8) > k_{obs}(13)$

Conclusions

- The rate constant for the initiator (8) is higher than the rate constant for the initiator (13)
- Initiator (8) is difunctional
- Initiator (13) is monofunctional

Future
End Capping

Monofunctional: I-MM* + RNCO → I-MMM-R

Difunctional: *MM-I-MM* + RNCO →R-MMM-I-MMM-R

RNCO= isocyanate
R: NMR or UV

Complete Kinetics Study