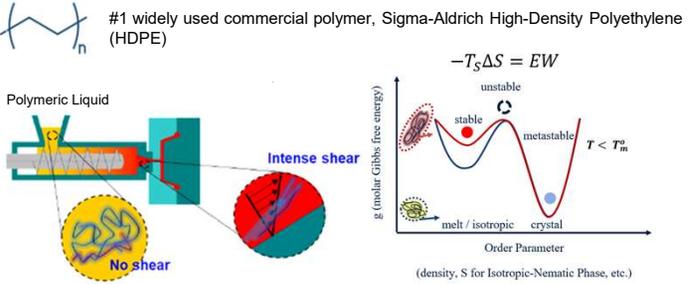


# Important Role of Energy Conversion Factor ( $E$ ) on Kinetics of Polymer Crystallization

## MOTIVATION: FLOW INDUCED CRYSTALLIZATION

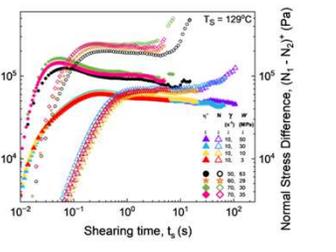
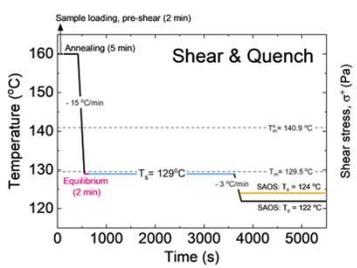
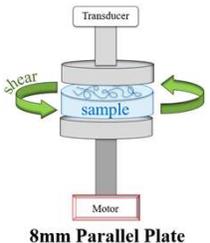
- Expand the shear-rate windows in industrial extrusion, compounding, and molding operations
- Link chain alignment to crystal precursor formation using  $E$  to enable predictable process control.
- Provide a "dial" for industry to tune crystallization kinetics across polymer manufacturing



## METHODS: USING RHEOLOGY AS TOOL

### Ares G2 - Rheological Characterization

- Strain controlled experiments in the linear regime to minimize stress on HDPE
- All pucks sheared at 129°C and monitored at  $T_C = 122, 124$  °C and with 0.01 strain and 1 rad/s angular frequency
- Recorded storage & loss moduli, and crossover times to monitor crystallization kinetics before and after shear

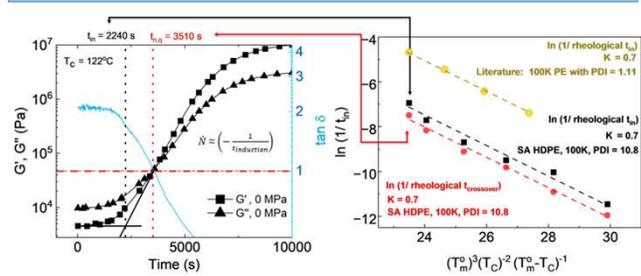


**Evan Moffett<sup>1</sup>, Arshiya Bhadu<sup>1</sup>, Alicyn M. Rhoades<sup>2</sup>, Ralph H. Colby<sup>1</sup>**  
<sup>1</sup> Dept. of Materials Science and Engineering, Penn State University, University Park, PA 16802, US  
<sup>2</sup> School of Engineering, Penn State Behrend, Erie, PA 16563, US

## ABSTRACT

Shearing a molten polymer can lower the configurational entropy of chains and the free energy nucleation barrier. Shear experiments are limited due to elastic instabilities like edge fracture. Edge fracture was delayed by stretching the high molecular weight chains and forming stable crystal precursors that expand the applicable shear rate range from 1 – 5 s<sup>-1</sup> up to 70 s<sup>-1</sup>. Specific work ( $W$ ) is assumed to be the control variable for acceleration in nucleation but that is not the case when a wide range of shear rates is utilized. Instead, the energy conversion factor ( $E$ ) multiplied by  $W$  is the real control variable that links processing conditions to predictive structure development for industrial polymers such as HDPE and PEEK..

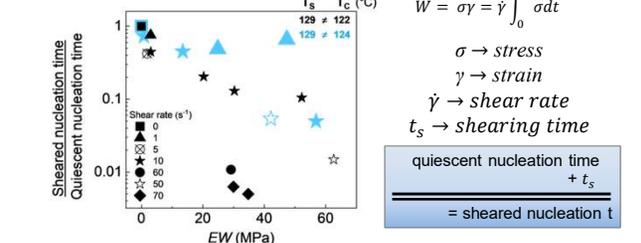
## BASELINE VALIDATION



- Quiescent (not sheared sample) crystallization kinetics from rheology and thermal analysis
- Slope matches literature value of  $K=0.7$

## SPECIFIC WORK NOT THE CONTROL VARIABLE

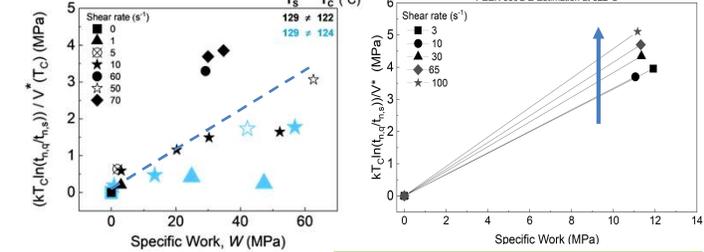
- Expected response after shear is a **linear** decrease in the nucleation time as the applied specific work increases



- The deviation suggests specific work is not the only factor at play quantifying acceleration in crystallization kinetics as assumed in literature

## EW IS THE CONTROL VARIABLE

- $E$  can be estimated for these shearing conditions and temperatures by calculating  $V^*$  then using the slope

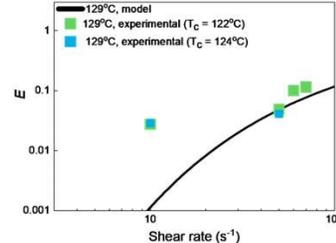


$$V^*(T_C) = \frac{K (T_m^0)^3 k}{\Delta H_f} \left( \frac{T_m^0}{(T_m^0 - T_C) T_C} \right)^2$$

$$EW = \frac{k T_C}{V^*(T_C)} \ln \left( \frac{\text{Quiescent Nuc. Time}}{\text{Sheared Nuc. Time}} \right)$$

- The mean slope of the line estimates  $E = 0.036$  which is the approximate weight percent of long chains (2.9%) in HDPE
- Preliminary data for PEEK shows that each linear slope ( $E$ ) increases with shear rate, while  $W$  is a consequence of shearing time

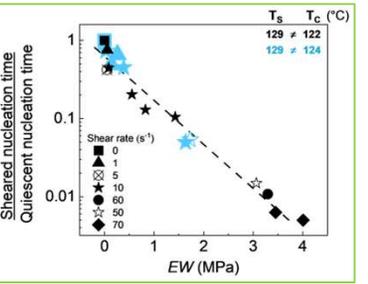
$$E = \frac{\int_0^\infty N_{\text{stretched}} w_N dN}{\int_0^\infty w_N dN} \sim \exp \left( \frac{-1}{N_{\text{max}} \sqrt{\dot{\gamma} t_0}} \right)$$



- This model states the chains that are  $N_{\text{max}}$  or greater stretch first under shear and impact the subsequent energy conversion into reducing the energetic barrier to crystallize
- As the  $\dot{\gamma}$  increases,  $N_{\text{stretched}}$  decreases (in chain length) and more chains get stretched in shear.

## CONCLUSIONS

- The experimental  $E$  value exceeds the model's prediction due to the influence of long polymer chains, which facilitate the alignment and stretching of shorter chains, enhancing energy conversion
- Acceleration of crystallization is reduced to a common curve as a function of  $EW$



## CONCLUSIONS

- $E$  scales with the fraction of long chains that orient under shear, while long-chain alignment promotes stretching of shorter chains, linking how processing energy translates to crystallization kinetics
- Together,  $W$  and  $E$  form a material-specific control parameter for predicting crystallization behavior under new industrial processing conditions
- This framework is transferable across multiple industrial polymers, HDPE and PEEK