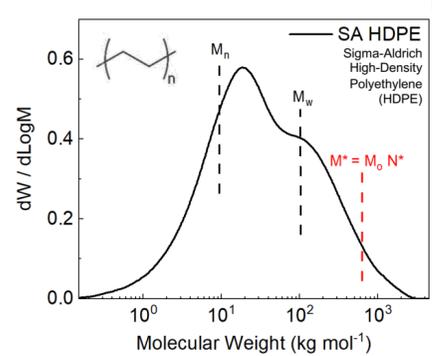


# WHEN FLOW CREATES ORDER: NEMATIC ALIGNMENT AND FORM BIREFRINGENCE IN SHEAR FOR HIGH-DENSITY POLYETHYLENE MELTS

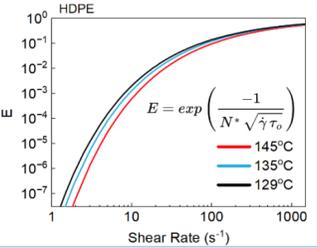
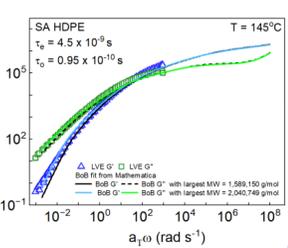
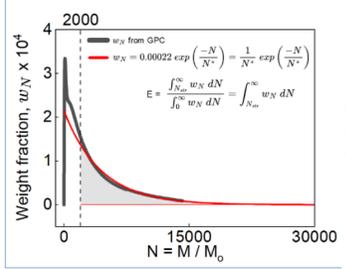


## INTRODUCTION & MOTIVATION

- Complex flows induced during polymer processing cause changes in structural morphology and affect the properties of the processed polymer.
- Shearing of a semi-crystalline polymer accelerates its crystallization kinetics but its fundamental pathway is unknown; here we show that liquid crystalline alignment is a key step along that pathway.
- Using only the molecular weight distribution of a polymer one can determine the fraction of chains that stretch at a particular shear rate and temperature ( $E$ )



$$T_s \Delta S = E(T_s) W$$



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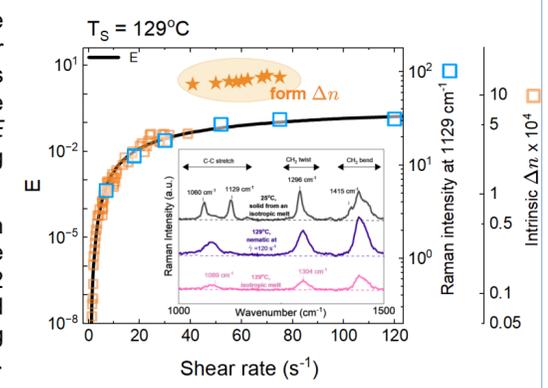
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### ABSTRACT

Making use of the exponential character of the high molecular weight tail of high density polyethylene allows quantification of the fraction of chains that get stretched in shear flow, which tracks with measured birefringence and Raman intensity. At high enough shear rates, apparent viscosity and birefringence show the shear rate dependence of chains that exhibit nematic alignment. In the nematic regime, a strong increase in birefringence occurs accompanied by a failure of the linear stress-optical rule, suggesting that form birefringence results from nematic alignment which was confirmed using optical techniques.

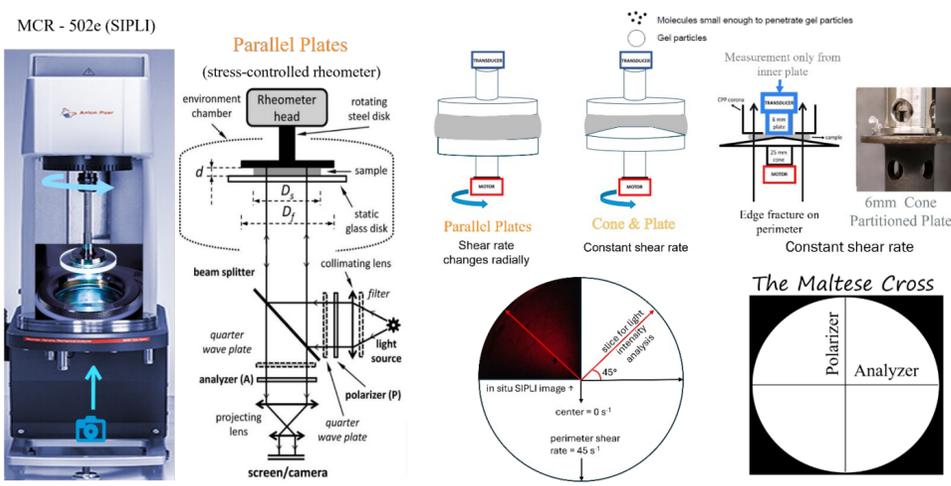
### ENERGY CONVERSION FACTOR (E) & FLOW-INDUCED NEMATIC IN HDPE

- Both birefringence and the Raman peak for consecutive all trans conformations follow the expected increase in  $E$  from stretching of long chains.
- The viscosity as a function of shear rate shows the Marrucci slope of -1/2 expected of nematic liquid crystals when strong birefringence occurs (form).



## METHODS

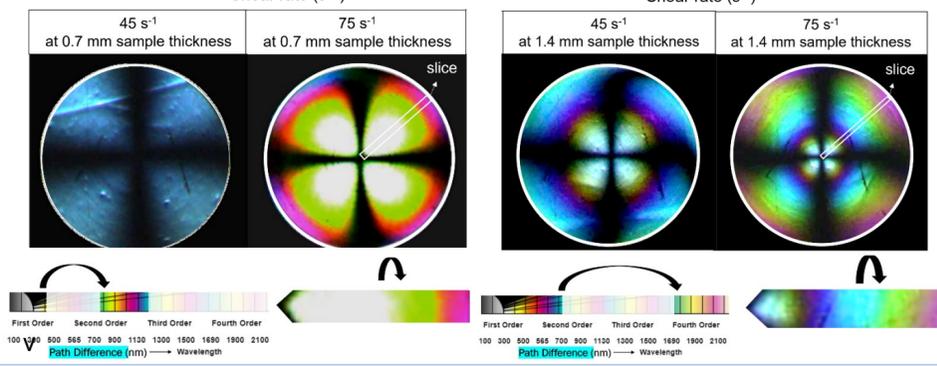
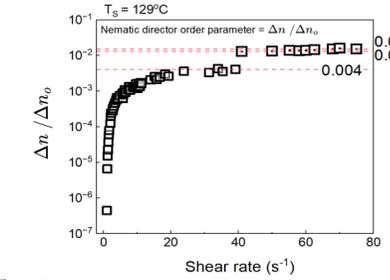
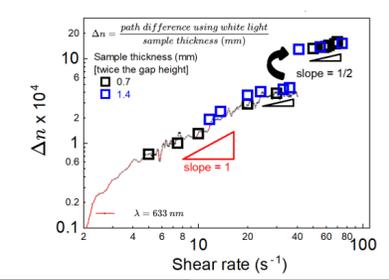
- Gel permeation chromatography for determining molecular weight distribution of HDPE
- Rheological arsenal for rheo-optical measure of birefringence in shear flow and viscosity measurements.



F. Snijkers, D. Vlassopoulos (2011) *J. Rheol.* **55** (6) 1167–860.  
Mykhaylyk, O. O.; Warren, N. J.; Parnell, A. J.; Pfeifer, G.; Laeuger, J. (2016) *J. Polym. Sci., Part B: Polym. Phys.* **54**, 2151–2170.

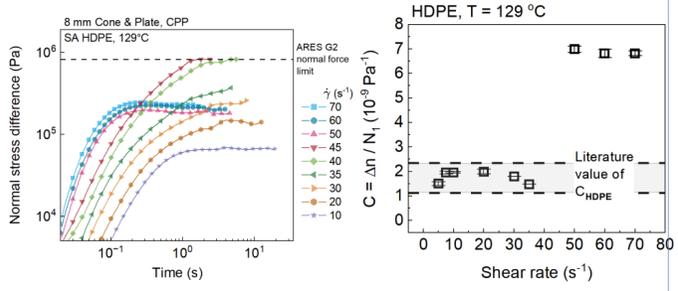
## BIREFRINGENCE EVALUATION & NEMATIC ORDER PARAMETER

- Birefringence also shows the Marrucci slope of 1/2 expected of nematic liquid crystals.
- Emergence of form birefringence leads to a step change in birefringence.
- When the birefringence makes a sudden increase, 1.3% of the HDPE melt is nematic which increases with increasing shear rate up to 1.5%.



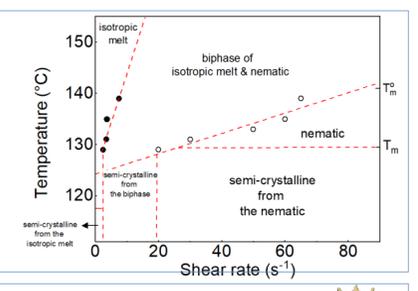
## FORM BIREFRINGENCE & STRESS-OPTICAL COEFFICIENT

- Normal stresses drop once strong nematic alignment occurs.
- The stress-optical coefficient (C) of HDPE increases to lyotropic liquid crystal values.



## CONCLUSIONS

- Processing phase diagram for HDPE based on the fraction of chains that stretch at a given shear rate and temperature.
- Applicable to most commercial polymers if MWD is known.



## ACKNOWLEDGEMENTS

Jerry Mcgraw for GPC collection of HDPE.