## Nonlinear polymer rheology:

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#### PREFACE

#### INTRODUCTION

#### PART ONE LINEAR VISCOELASTICITY AND EXPERIMENTAL METHODS

#### 1. Phenomenological description of linear viscoelasticity (LVE)

- 1.1 Basic modes of deformation
- 1.2 Linear responses
- 1.3 Classical rubber elasticity theory

#### 2. Molecular characterization in LVE regime

- 2.1 Dilute limit
- 2.2 Entangled state
- 2.3 Molecular-level descriptions of entanglement dynamics
- 2.4 Temperature dependence

#### **3. Experimental Methods**

- 3.1 Shear rheometry
- 3.2 Extensional rheometry
- 3.3 Rheo-optical (in situ) methods
- 3.4 Advanced rheometric methods

#### 4. Characterization of deformation field

- 4.1 Basic features in simple shear
- 4.2 Yield stress in Bingham type (yield-stress) fluids
- 4.3 Cases of homogeneous shear
- 4.4 Particle tracking velocimetry (PTV)
- 4.5 Single molecule imaging velocimetry (SMIV)
- 4.6 Other methods

## 5. Improved rheometric apparatuses

- 5.1 Linearly displaced co-cylinder for simple shear
- 5.2 Cone-partitioned plate for rotational shear
- 5.3 Other forms of large deformation
- 5.4 Conclusion

# PART TWO YIELDING – PRIMARY NONLINEAR RESPONSES TO ONGOING DEFORMATION

## 6. Wall slip – Interfacial yielding

- 6.1 Basic notion of wall slip in steady shear
- 6.2 Stick-slip transition in stress-controlled mode
- 6.3 Wall slip during startup shear Interfacial yielding
- 6.4 Relationship between slip and bulk shear deformation
- 6.5 Molecular evidence of disentanglement during wall slip
- 6.6 Uncertainty in boundary condition
- 6.7 Conclusion

## 7. Yielding during startup deformation: from elastic deformation to flow

- 7.1 Yielding at Wi < 1 and steady shear thinning
- 7.2 Stress overshoot in fast startup shear
- 7.3 Nature of steady shear
- 7.4 From terminal flow to fast flow under creep: entanglement-disentanglement transition
- 7.5 Yielding in startup uniaxial extension
- 7.6 Conclusion

## 8. Strain hardening in extension

- 8.1 Conceptual pictures
- 8.2 Origin of "strain hardening" in uniaxial extension
- 8.3 True strain hardening: non-Gaussian stretching from finite extensibility
- 8.4 Different responses of entanglement to startup extension and shear
- 8.5 Conclusion
- 8.A Conceptual and mathematical account of geometric condensation

#### 9. Shear banding in startup and oscillatory shear: PTV observations

- 9.1 Shear banding after overshoot in startup shear
- 9.2 Overcoming wall slip during startup shear
- 9.3 Shear banding in LAOS

## 10. Strain localization in pressure-driven extrusion, squeezing, and planar extension

- 10.1 Capillary rheometry in rate-controlled mode
- 10.2 Instabilities at die entry
- 10.3 Squeezing deformation
- 10.4 Planar extension

#### **11. Different modes of structural failure during uniaxial extension**

- 11.1 Tensile-like failure at low rates
- 11.2 Shear yielding and necking-like strain localization
- 11.3 Rupture without crosslinking: where is disentanglement?
- 11.4 Strain localization vs. steady-flow: SER vs. FSR
- 11.5 Role of long chain branching

11.A Analogy between capillary rheometry and filament stretching rheometry

# PART THREE DECOHESION AND ELASTIC YIELDING AFTER LARGE DEFORMATION

## 12. Elastic yielding in stepwise simple shear

- 12.1 Strain softening after large step strain
- 12.2 PTV revelation of non-quiescent relaxation: localized elastic yielding
- 12.3 Quiescent and uniform elastic yielding
- 12.4 Arrested wall slip: elastic yielding at interfaces
- 12.5 Conclusion

## 13. Elastic breakup in stepwise uniaxial extension

- 13.1 Rupture-like failure during relaxation at low magnitude or low rates ( $Wi_R < 1$ )
- 13.2 Shear-yielding induced failure upon fast stepwise extension ( $Wi_R > 1$ )
- 13.3 Nature of the elastic breakup probed by infrared measurements
- 13.4 Primitive phenomenological explanations
- 13.5 Stepwise squeeze and planar extension

## 14. Finite cohesion and the role of chain architecture

- 14.1 Cohesive strength of an entanglement network
- 14.2 Enhancing cohesion barrier with long-chain branching to prevent structural breakup

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## **15. Homogeneous entanglement**

- 15.1 What is chain entanglement?
- 15.2 When, how and why disentanglement occurs
- 15.3 Criterion for homogeneous shear
- 15.4 Constitutive non-monotonicity
- 15.5 Metastable nature of shear banding

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- 16.1 Introduction: the tube model and its predictions
- 16.2 Essential ingredients in formulation of a new molecular picture
- 16.3 Overcoming finite cohesion after step deformation: Quiescent or not
- 16.4 Forced yielding during startup deformation: stress overshoot
- 16.5 Interfacial yielding by disentanglement
- 16.6 Effect of long chain branching
- 16.7 Decohesion in startup creep: entanglement-disentanglement transition
- 16.8 Emerging microscopic theories of Sussman and Schweizer
- 16.9 Further tests to reveal the nature of polymer deformation
- 16.10 Conclusion

#### 17. "Anomalous" phenomena

- 17.1 Essence of rheometric measurements: isothermal condition
- 17.2 Internal energy buildup and non-Gaussian extension
- 17.3 Breakdown of time-temperature superposition during transient response: shear and extension
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- 17.5 Lack of universal nonlinear responses: solutions vs. melts
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- 18.2 Confusion about local and global deformation
- 18.3 Molecular network paradigm

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- 19.1 Relationship between wall slip and banding: a rheological-state diagram
- 19.2 Modeling of continuum fluid mechanics of entangled polymeric liquids
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