

UNIVERSITY OF UTAH GRADUATE SCHOOL

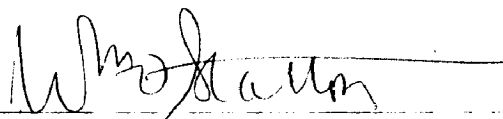
FINAL READING APPROVAL

To the Graduate Council of the University of Utah:

I have read the dissertation of Richard Patrick Wool in its final form and have found that (1) its format, citations, and bibliographic style are consistent and acceptable; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the Supervisory Committee and is ready for submission to the Graduate School.

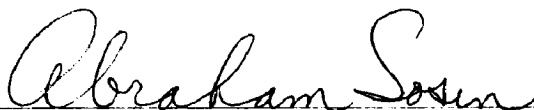
Date

Nov 15, 1974



William O. Statton
Member, Supervisory Committee

Approved for the Major Department



Abraham Sosin
Chairman/Dean

Approved for the Graduate Council

Sterling M. McMurrin
Dean of the Graduate School

UNIVERSITY OF UTAH GRADUATE SCHOOL

SUPERVISORY COMMITTEE APPROVAL

of a dissertation submitted by

RICHARD PATRICK WOOL

I have read this dissertation and have found it to be of satisfactory quality for a doctoral degree.

Nov-15, 1974
Date

William O. Statton
William O. Statton
Chairman, Supervisory Committee

I have read this dissertation and have found it to be of satisfactory quality for a doctoral degree.

Nov-15, 1974
Date

K. L. DeVries
K. L. DeVries
Member, Supervisory Committee

I have read this dissertation and have found it to be of satisfactory quality for a doctoral degree.

Nov 15, 1974
Date

R. H. Boyd
R. H. Boyd
Member, Supervisory Committee

I have read this dissertation and have found it to be of satisfactory quality for a doctoral degree.

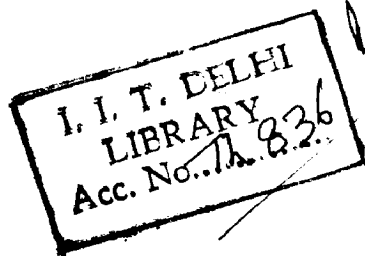
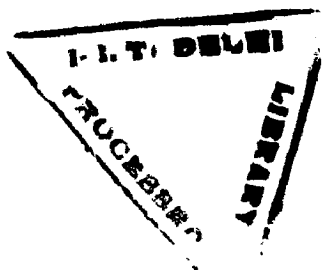
Nov. 15, 1974
Date

S. M. Breitling
S. M. Breitling
Member, Supervisory Committee

I have read this dissertation and have found it to be of satisfactory quality for a doctoral degree.

Nov. 15, 1974
Date

Fritz Luty
Fritz Luty
Member, Supervisory Committee



16/4/82

TH
539.38:678
WOO - M

ACKNOWLEDGMENTS

The author wishes to extend his gratitude and appreciation to those who aided in the completion of this dissertation.

To my research advisor and committee chairman, Professor Bill Statton, I offer my sincerest thanks for introducing me to this area of research and being instrumental in providing financial assistance for the duration of my Ph.D. studies. His enthusiasm, friendliness, astute advice in all matters and attitude of positive reinforcement towards an often beleaguered student makes me proud of my association with this gentleman and teacher.

The other members of my Ph.D. committee, Professors R. H. Boyd, K. L. DeVries, S. M. Breitling and F. W. Luty, played an active role in experimental and theoretical development, for which I will always be grateful and especially appreciative of their generously given time in my academic affairs.

For their jovial compliance and oftentimes interesting intellectualizations, I thank my fellow students, Des Penny, Krishna Mocherla, Michael Quinlan, Greg McKenna and Suneet Sikka.

Appreciation is also expressed to Dr. Henning Kausch for his many interesting discussions and experimental involvement.

This dissertation is dedicated to my wife, Deborah, for her innumerable sacrifices, love, constant companionship, and assistance. To her, my sincerest appreciation and profound thanks are offered.

Finally, I am grateful for a perspective of this dissertation
offered by the verse:

*The pages swarm before me
Telling their mighty tale
Of man's mundane madness
His intellect doth assail.*

ABSTRACT

The mechanisms underlying the phenomenon of vibrational frequency shifting in stressed polymers were investigated. It was discovered that mechanisms involving geometric or conformational changes of molecular structure coupled with the reduction of force constants associated with molecular bonds and angles were the major contributors to frequency shifts in the infrared spectrum. New dynamic infrared techniques were developed to investigate the molecular mechanics of polymers subjected to any macroscopic deformation. Subtle changes of frequency and intensity obtained while the polymer was being stressed made it possible to determine time-dependent molecular stress distributions, orientation changes, conformational variations and bond rupture processes. By using polarized infrared, a method was also developed to determine the time-dependent orientation distribution of bonds at any stress level in the molecular stress distribution. Thus a method was available to correlate the molecular mechanics in terms of the macroscopic deformation. Time, morphology, thermal and strain histories also became variables in this study. These methods were then applied to investigate the molecular mechanics of highly oriented viscoelastic polypropylene during stress relaxation and creep. A mechano-chemical viscoelastic model was developed based on chain length distributions and linear viscoelasticity. Calculated intensities and frequency variations based on this model were found to be in good qualitative agreement with the observed spectra. A comparison of the

molecular mechanics of stress relaxation and creep showed them to be opposite in behavior in most respects, e.g., orientation, bond rupture, molecular stress distributions, etc. Tobolsky-Eyring reaction rate theory applied to bond rupture was successfully correlated with the viscoelastic model and the spectral behavior. The effects of thermal and strain histories are also presented. Dynamic infrared techniques are considered very useful in evaluating molecular responses as a function of various loading conditions.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	iv
LIST OF FIGURES	ix
LIST OF TABLES	xiv
ABSTRACT	xv
CHAPTER	
I. INTRODUCTION	1
II. INFRARED OF POLYMERS	4
2.1 Basic Theory of Infrared	4
2.1.1 Harmonic Oscillator Selection Rules	8
2.2 Infrared of Polyatomic Systems	10
2.2.1 Introduction	10
2.2.2 The Secular Equation	12
2.2.3 Solution of the Secular Equation	15
2.3 Vibrational Analysis of Irregular Polymers	18
III. EXPERIMENTAL OPERATION	23
3.1 Equipment Design	23
3.2 Experimental Operation	27
IV. INFRARED OF STRESSED POLYMERS	30
4.1 Deformed Bands	30
4.1.1 The Nature of the Deformed Band	34
4.2 Variation of Force Constants	35
4.3 Conformational Effects	45
4.4 Density of State and Defects	51
4.5 Anharmonicity and Phonon Interactions	58
4.5.1 Conclusions on the Nature of Band Deformation	59
4.6 Determination of Molecular Stress Distributions	59
4.6.1 Determination of $F(\nu)$	64

TABLE OF CONTENTS (continued)

	<u>Page</u>
4.7 Infrared Band Deformation Modes	65
4.7.1 Separation of Variables	68
V. STRESS RELAXATION	73
5.1 Morphology of Polymers	74
5.2 Initial Observations	83
5.2.1 Summary of Initial Observations.	91
5.3 A Viscoelastic Analogy	91
5.3.1 The Viscoelastic Chain	93
5.4 Bond Rupture	97
5.4.1 Effective Strain Distribution	102
5.4.2 The Molecular Stress Distribution	103
5.4.3 Constant Frequency Intensities	104
5.5 Bond Fracture Determination	106
5.5.1 Conclusions on Bond Fracture	110
5.6 Experimental and Calculated Intensities	111
5.6.1 Summary	122
VI. ORIENTATION EFFECTS DURING STRESS RELAXATION	123
6.1 Average Orientation Changes	123
6.2 Spatial Stress Distributions	125
6.2.1 Chain Orientation and Intensities	126
6.3 Determination of θ	132
6.4 Behavior of $R(\sigma_i, t)$ During Stress Relaxation of the 975^{-1} cm^{-1} band	132
6.4.1 Summary of Orientation Analysis	135
6.5 The Helix Bands	136
6.5.1 Sensitivity of the Helix Bands	136
VII. STRAIN HISTORY	147
7.1 Strain Ramp and Stress Relaxation	147
7.2 Repeated Loading	152
7.3 Effect of Annealing	160

TABLE OF CONTENTS (continued)

CHAPTER	<u>Page</u>
VIII. CREEP	166
8.1 Molecular Stress Distributions	166
8.2 Fracture of Bonds	178
8.2.1 Summary of Bond Fracture During Creep	185
8.3 Orientation and Helix Regularity	185
8.4 A Note on Fracture and Orientation	187
IX. SUMMARY AND CONCLUSIONS	193
9.1 Research Objectives	193
9.2 Basics and Techniques	194
9.3 Stress Relaxation and Creep	196
9.3.1 A Note on Morphology and Continuum Mechanics	198
9.4 Merits and Limitations	199
APPENDIX	
A. FLOW DIAGRAM OF SERVO-CONTROLLER	201
B. 1. DECONVOLUTION PROGRAM	203
2. CALCULATES STRESS DISTRIBUTIONS DURING STRESS RELAXATION	206
3. CALCULATES STRESS DISTRIBUTIONS DURING CREEP . . .	207
REFERENCES	208
VITA	213