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William O. Statton
Chairman, Supervisory Committee

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Nov 15, 1974
Date

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
Member, Supervisory Committee

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

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S. M. Breitling
Member, Supervisory Committee

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Nov. 15. 1974
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Fritz Luty
Member, Supervisory Committee

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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.

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