

## Response to “Comment on Birefringence in the Softening Zone”

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We have difficulty believing that the viscoelastic behavior of polymers can be interpreted in terms of distinct “rubbery” and “glassy” components, however these putative entities are assumed to interact. As stated previously,<sup>1</sup> “The interplay of forces in a dynamically correlated system such as polymer melts may be too complicated for any simple analysis to be correct.” Osaki and co-workers have employed a stress-additivity assumption (eq 2a in Inoue and Osaki<sup>2</sup>), originally proposed by Read,<sup>3</sup> to describe viscoelastic data for polymers. Their model can only be tested by comparison to experiment.

The ability to fit data by assuming additivity of the stresses does not corroborate this assumption; it is a consequence of the assumption. Our demonstration<sup>1</sup> that stress birefringence data for polyisoprene can also be fit by assuming the opposite, that the internal strains are additive, was intended to emphasize the ambiguity of the IO method. As we stated earlier:<sup>1</sup> “The work described herein is not meant to suggest that an interpretation based on the summation of strains is necessarily valid.”

The insight provided by the IO method is the relative contributions of hypothetical rubbery and glassy components to the viscoelastic spectrum; the validity of the IO analysis reside solely in this information. However, as we showed earlier,<sup>1</sup> for polyisoprene, the relative magnitudes of these putative contributions contradict known experimental facts.

The most significant implication of IO<sup>4</sup> is that the glassy component dominates the viscoelastic response at frequencies well into the rubbery plateau region. This result is at odds with the change in sign of the imaginary part of the strain optical coefficient<sup>4</sup> and the decay of the glassy compliance,<sup>5,6</sup> both of which occur in the high-frequency end of the softening zone. It also contradicts the behavior of the local segmental relaxation function, which becomes negligible in the middle of this region of the spectrum.<sup>7</sup>

We also point to creep recovery experiments employing the “encroachment effect”,<sup>8,9</sup> which enables removal of all viscoelastic modes other than those involving local

segmental motion. Such experiments show the prominence of the chain modes in the softening zone. Nevertheless, as we discussed previously,<sup>1</sup> the IO analysis<sup>4</sup> would suggest that the glassy component makes the dominant contribution at these frequencies. Although IO do not attempt to explain the conflicts of their model with empirical observations, these discrepancies led us to propose, “reexamination of the assumption of stress additivity and any inferences derived from it.”<sup>1</sup>

Lastly, although it diverts from the important aspects of this debate, in response to IO,<sup>2</sup> of course we agree that the modulus of a Maxwell model, and indeed any mechanical model with parallel elements, can be expressed as the sum of contributions from the parallel elements. This is trivial, but the extension of simple analogs to the behavior of real materials is not. The assertion<sup>2</sup> that our expression for  $D_G''/D$  is independent of molecular weight, and thus a “serious defect”, is incorrect. From eq 19 in Mott and Roland,<sup>1</sup> we obtain

$$D_G''/D' = \frac{\frac{C_R O'}{(O^2 + O'^2)D'} - 1}{\frac{C_R}{C_G} - 1} \quad (1)$$

The dynamic strain optical coefficients,  $O'$  and  $O''$ , are both molecular-weight-dependent, and thus the left-hand side of eq 1 is as well. Notwithstanding these details, our strain-additivity analysis was intended, not so much to be an improvement on the method, but rather to call the entire approach into question.

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## References and Notes

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