A Response to the Comment on "Molecular Modeling of Polymers. 7. Ab Initio Demonstration of Torsional Angle Cooperativity in Linear Chains by Molecular Dynamics" by D. C. Doherty and A. J. Hopfinger (*Macromolecules* 1990, *23*, 676–678)

Dr. Robert J. Meier has presented significant and thought-provoking points concerning our manuscript. We appreciate the time and effort he has given to studying the information we report in the paper.

From our perspective, the comments made by Dr. Meier fall into two classes: first, points of clarification and, second, possible interpretations of the data. We first address points of clarification. Additional details of the simulation experiments are given in the following: *Computer Simulation of Polymers*; Roe, R. J., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; p 55. Exhaustive details of the subject and other molecular dynamics simulations of chain molecules are given in D. C. Doherty's dissertation, which is in final preparation.

The term ab initio generally denotes first principle and/or fundamental property. Ab initio is usually associated with quantum mechanics. However, this term is not exclusively reserved for the description of a quantum mechanics calculation. We used ab initio to emphasize that torsion angle cooperativity is a fundamental property of *n*-alkane chains according to full-Cartesian molecular dynamics, MD.

The simulations in going from the orthorhombic to the hexagonal phase consist of an equilibration period followed by 5-ps trajectories over each of six coupled microstates uniformly distributed, with respect to geometry, over orthorhombic to hexagonal transition phase space. We believe the corresponding correlation functions are meaningful because the microstates are coupled and because full-Cartesian MD has been employed. The system can completely "relax" at any point along the trajectory. Additional calculations, subsequent to the published work under discussion, indicate the essential features of the correlation functions remain the same to those published for simulations limited to a single microstate, and they do not change for differing equilibration conditions. The information content in each of the correlation functions is in the 0–2-ps regime as Dr. Meier infers.

We stress that the simulation temperature is not necessarily quantitatively scaled to the actual temperature of a system. The simulation temperature is dependent upon the force field employed in the simulation.

The *demonstration of torsion angle cooperativity*, diagonals of near-constant shading in Figure 2, is prevalent over the entire 2.5-ps period reported in Figure 2 and, in fact, persists over the full 5-ps trajectory. The *extent* of cooperativity in any subdomain time period within the trajectory is uneven, as is characteristic of MD simulations. The most pronounced diagonals end near 1 ps as Dr. Meier points out.

Regarding the interpretation of MD data, we note that torsion angle cooperativity could be involved in the structural phase transition mechanism of *n*-alkane chain molecules. However, we do not wish to imply that this is, in fact, the case based on our simulation data. It is worth noting that we have done analyses of the normal-mode eigenvectors at various points along the MD trajectories. We hoped to identify characteristic modes of motion perhaps promoting, or at least indicative of, the structural transition. This is in line with Dr. Meier's comments and viewpoint. Unfortunately, no characteristic eigenvectors have been found at this time.

Overall, we think the data presented in our paper demonstrate that torsion angle cooperativity occurs in chain molecules and that such cooperativity could be involved in structural transition mechanisms.

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Received February 2, 1991

0024-9297/91/2224-1693$02.50/0