Goldenfeld and Halley Respond: We were aware, as Petschek has pointed out, that free-end boundary conditions would give a different result and that if they are used, then no phase transition results in the model. It is clear that if free-end boundary conditions were used, then the phonon modes of the straight parts of the chain would be coupled to the phonon modes of the coiled parts so that the assumptions of fixed boundary conditions and of no transmission of phonon modes from straight to coiled parts of the chain are closely interdependent. We agree that, if one waits long enough, then such transmission must occur so that on long enough time scales our model must break down. Thus on long time scales, we believe that a correct model can be expected not to exhibit a true phase transition in agreement with the extremely well-known theorems on phase transitions in one dimension to which Petschek alludes and to which we referred in our Letter.[1] This is what we intended to convey in the following words quoted from our Letter: "The purpose of this Letter is to suggest that rod-to-coil transformations in single-stranded polymers can actually be very close to being true phase transitions."

The model presented in our Letter is intended to describe the behavior of the system, not in equilibrium, but on a time scale which we believe can be of the order of the experimental time scales. Below, we present a more detailed argument for why we believe that the model can account for experiments on macroscopic time scales. We distinguish the following time scales: τ_p, the transit time for a phonon through a straight part of the chain; τ_e, the experimental time; τ_G, the nucleation time for a gauche bond; τ_D, the time for a gauche bond to diffuse the length of the whole chain; and τ_L, the time for phonon to leak out of a straight part of the chain. We will argue that under experimentally credible circumstances, the following hierarchy can occur, leading to circumstances in which our model will approximately describe the experiments:

$$\tau_D > \tau_e \gg \tau_L \gg \tau_G \gg \tau_p.$$

The key requirement is that $\tau_L \gg \tau_G$ so that the equilibrium distribution of gauche bonds in the chain is governed by the equilibrium distribution of phonons calculated without regard for transmission across the boundaries between straight and coiled parts as our model assumes. We note that τ_G can be quite short, being of order $(\tau_p/L_s)e^{\Delta\beta}$, where L_s is the length of a straight part of the chain and Δ is the energy cost of creating a gauche bond as defined in the Letter. Thus if the phonons in the straight parts of the chain can be defined at all then the needed inequality can be achieved if Δ is of the order of $k_B T$. If, instead of the above hierarchy, one has $\tau_e \gg \tau_D$ then we expect that the full equilibration of the chain will result in no true phase transition. But τ_D is a macroscopic time. It may be that the hysteresis observed in the experiments is due to competition between τ_e and τ_D. If the key inequality $\tau_L \gg \tau_G$ is not satisfied then our model breaks down as a description. In that case, however, it cannot be correct simply to change the boundary conditions in the calculation of the phonon spectrum of the straight parts of the chain as Petschek seems implicitly to suggest, since one must then confront the whole problem of the harmonic spectrum of the disordered chain. Finally, we do not expect these conclusions to be altered by the solvent for the same reasons which we gave in the Letter.

We wish to take this occasion to thank Argonne National Laboratory for hosting us while we did some of the work.

Nigel Goldenfeld
Loomis Laboratory of Physics
Urbana, Illinois 61801

J. W. Halley
School of Physics and Astronomy
University of Minnesota
Minneapolis, Minnesota 55455

Received 10 December 1985
PACS numbers: 64.60.Cn, 36.20.Ey

[1]N. D. Goldenfeld and J. W. Halley, Phys. Rev. Lett. 55, 730 (1985).