Coherent Scattering from Polymer Melts

In a recent paper, Richter et al.[1] report measurements of the dynamic coherent structure factor $S_{coh}(q,t)$ of a labeled polydimethylsiloxane melt and the results of a computer simulation of a polymer melt consisting of very short chains. They conclude that the theory of reptation[2-5] is in qualitative disagreement with their results and that "a new approach to the dynamics of entangled polymers is called for."

We start by drawing attention to Eq. (5b) of Ref. 1 where the term $q^2D^2/36$ has been incorrectly omitted (here D is the tube diameter). This term is not small compared to the one retained, and the correct expression (Eqs. 3.12–3.14 of Ref. 3) is plotted in Fig. 1 with the choice of parameters discussed below. There is a strong q dependence, contrary to the claims[6] of Richter et al.

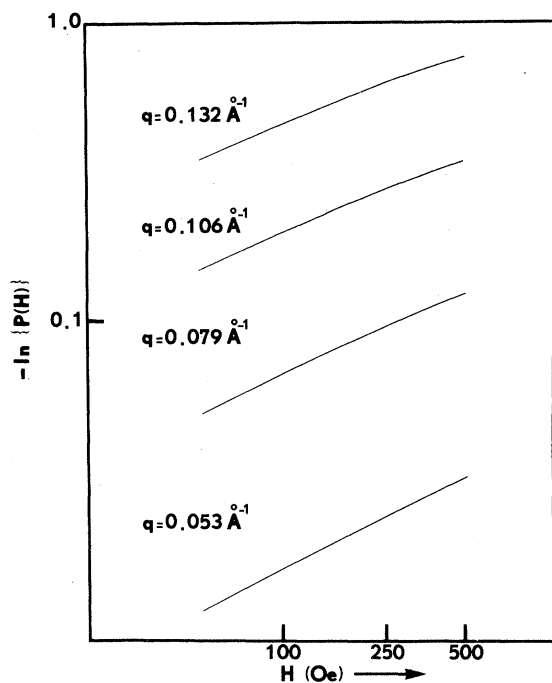The values of the parameters l and W, in the notation of Ref. 1, were obtained from previous

experiments.[7,8] We estimate D to be around 40 Å, using viscoelastic data[5] and the Doi-Edwards theory.[4,9] It is clearly stated in Ref. 3 that for $qD > 1$ the simple Rouse behavior is recovered. The values of qD in the experiment lie in this regime. Thus the comparison by Richter et al. of the reptation formulas with experiment is rendered otiose. The only criterion for the onset of characteristic reptative effects, however, is that R, the polymer size, be larger than D, which is not the range of validity $(1/R \ll q \ll 1/D)$ of Eqs. 3.12–3.14 of Ref. 3.

For Richter et al. to retain their conclusion, they must show that the tube diameter is much less than 20 Å so that $qD < 1$. This would contradict a large body of experimental data.[4,5] In conclusion, the experiment does not appear to refute the existing theory.

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FIG. 1. Polarization decay $P(H) = S_{coh}(\vec{q},t)/S_{coh}(\vec{q},0)$ from Ref. 3, where H is the applied guide field and 100 Oe $\simeq 1.9 \times 10^{-9}$ sec.

[1]D. Richter, A. Baumgärtner, K. Binder, B. Ewen, and J. B. Hayter, Phys. Rev. Lett. 47, 109 (1981).
[2]P. G. de Gennes, J. Chem. Phys. 55, 572 (1971).
[3]P. G. de Gennes, J. Phys. (Paris) 42, 735 (1981).
[4]M. Doi and S. F. Edwards, J. Chem. Soc. Faraday Trans. 2 74, 1789, 1818 (1978).
[5]W. W. Graessley, J. Polym. Sci. Polym. Phys. Ed. 18, 27 (1980); W. W. Graessley and S. F. Edwards, Polymer 22, 1329 (1981).
[6]Reference 1 states "There should be no q dependence if the nonexponential law, Eq. (5b), were valid!" It is not valid for the reasons discussed in the text, and also because the condition $(ql)^2(Wt)^{1/2} \gg 1$ is not satisfied in their experiment (notation of Ref. 1).
[7]L. K. Nicholson, Contemp. Phys. 22, 451 (1981).
[8]J. E. Tanner, K. J. Liu, and J. E. Anderson, Macromolecules 4, 586 (1971).
[9]This is consistent with de Gennes's estimate of about 200 monomer units for the entanglement length. See P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell Univ. Press, Ithaca, N.Y., 1979).