*Macromolecules* **1996,** *29,* 6349−6350

# Notes

## An Explanation for the Experimental Data on the Motion of Rings and Linear Chains in Melts and Microgels

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*Received February 13, 1996*

In this note, an explanation is proposed for an apparent paradox concerning the motion of polymer chains in melts. One set of experiments[1] shows that the diffusion constant for linear chains in microgels is very nearly the same as the diffusion constant for chains of the same length in a monodisperse melt or in a melt of very long chains. Since the radius of gyration for these chains is significantly larger than the mesh size for the microgels, it is reasonable to assume that the chain motion in these gels must occur by reptation.[2−4] The fact that the diffusion constant is nearly the same for chains in the microgels and in melts would seem to imply that linear chains also diffuse by reptation in melts.

On the other hand, a different set of experiments[5] have demonstrated that the zero shear viscosity for melts of ring polymers is nearly identical to the same quantity for linear polymer melts. These experiments suggest that the chain mobility for rings in melts is very similar to the chain mobility for linear chains. This seems inconsistent with the reptation model. Experiments on the diffusion of rings and linear chains in matrices of chains of various lengths[6,7] show a complicated dependence of the diffusion constant on the molecular weight of the probe polymers and the matrix polymers. Experiments,[6] which compare the diffusion constant for moderate size rings in linear chain melts with its value for linear chains in the same melts, find very little difference in the ring and linear chain diffusion constants. Still other diffusion experiments[7] in linear chain matrices conclude that the diffusion of high molecular weight rings is slower than the diffusion of the same molecular weight linear chains. However, the diffusion constants for the rings are higher, even in these experiments, than is predicted by reptation with constraint release.

Therefore, the ring data would seem to support the conclusion that diffusion in linear chain melts is dominated by a nonreptation mechanism, while the diffusion data for chains in microgels seemingly imply that diffusion in linear chain melts is dominated by reptation. Our proposed solution to this apparent paradox assumes that the diffusion of linear chains in melts is dominated by some mechanism other than reptation, as suggested by the ring data. We now show that this assumption is easily reconciled with the diffusion data for linear chains in microgels.

Curve a of Figure 1 is a typical plot of the diffusion constant of linear chains in monodisperse melts versus the chain molecular weight.[4] For small molecular weights, $D_{cm}$ has an $M^{-1}$ dependence. At a critical molecular weight, $M_c$, there is a crossover in the behavior of $D_{cm}$ to a $M^{-a}$ dependence, where $a$ is typically in the 2.0−2.1 range. A value of 2.1 is used for $a$ in the figure. Whatever the mechanism for diffusion might be in linear chain polymer melts, the dependence of the diffusion constant on molecular weight for this mechanism must be that which is observed experimentally for linear chain melts. While the argument presented here is not based on any particular assumption about the nature of this nonreptation mechanism, we have, in other work,[8−10] demonstrated that an $M^{-2.1}$ dependence can be obtained for the diffusion constant from a theory based on the lateral motion of the chains.

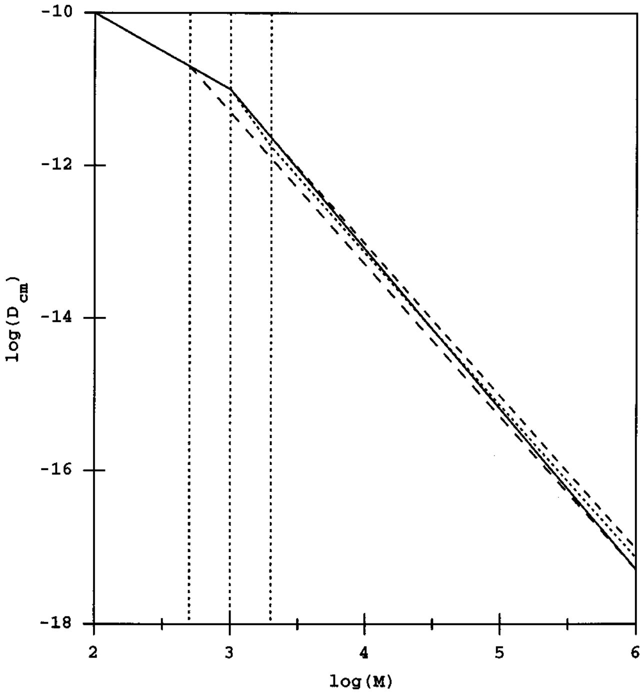

**Figure 1.** Typical dependence of $D_{cm}$ on molecular weight for linear chains in melts is plotted in curve a (solid curve). Possible dependences of $D_{cm}$ for linear chains in microgels are plotted in curves b (lower dashed curve), c (upper dashed curve), and d (dotted curve). The middle vertical dotted line indicates the value employed for $M_c$. The left vertical dotted line indicates the value used for $M_m$ for the case with $M_m$ less than $M_c$, and the right vertical dotted line indicates the value employed for $M_m$ for the $M_m$ greater than $M_c$ case.

Various possible plots for the dependence of the diffusion constant of linear chains in microgels are compared in Figure 1 with the melt diffusion constant. Curve b is appropriate for the case of a gel with a very small mesh size. In this case, the nonreptative motion of linear chains with molecular weights greater than some value, $M_m$, which is smaller than $M_c$ and is determined by the mesh size, is restricted by the presence of the gel, and the chains must diffuse by reptation. For $M$ larger than $M_m$, the diffusion constant has the $M^{-2}$ dependence consistent with reptation. As shown in the figure, this results in diffusion constants for linear chains in microgels which are not very

S0024-9297(96)00229-X CCC: $12.00

different from the melt values, as long as $M_m$ is not too different from $M_c$.

Curves c and d in Figure 1 indicate the expected possible behaviors of $D_{cm}$ for the case where $M_m$, the molecular weight at which the gel impedes the nonreptative chain motions, is larger than the critical molecular weight, $M_c$. For curve c, the diffusion constant has the same $M^{-2.1}$ dependence as the melts up to $M_m$. For molecular weights greater than $M_m$, the chains must reptate and the diffusion constant has an $M^{-2}$ dependence. Once again, only a slight difference between the diffusion constant in the melt and in the microgel is predicted in this case. Curve d differs only slightly from curve c. In our work on lateral chain motion,[8-10] it is argued that many chain correlated motions should play a significant role in the chain diffusion. Since the chains comprising the microgel have their motion restricted due to the cross-linking, this correlated motion contribution to $D_{cm}$ should be reduced in the microgel relative to the un-cross-linked melt. In the extreme case of zero correlated motion, the diffusion constant is predicted[8,10] to have an $M^{-2.3}$ to $M^{-2.5}$ dependence from $M_c$ to $M_m$. An $M^{-2.5}$ scaling is used in curve d. For $M$ greater than $M_m$, reptation must be the dominant mechanism, and $D_{cm}$ scales as $M^{-2}$. Once again, in this case, there is little difference between the value of the diffusion constant for long linear chains in the melt and in microgels, as long as the $M_m$ is not too much larger than $M_c$. If $M_m$ were much larger than $M_c$, then the extent of correlated motions in the microgel would not be very different from the melt for chains with $M$ much less than $M_m$, since the chain segments that make up the gel should have significant mobility over distances less than the mesh size. As $M$ approaches $M_m$, however, the restrictions on the mobility of the gel chains due to the cross-linking decrease the correlated contribution to the diffusion constant. The resulting value of $D_{cm}$ would again differ only slightly from the melt value for large $M$.

This argument demonstrates that the agreement between the diffusion constant for linear chains in melts and microgels does *not* imply that reptation is the dominant mechanism of motion for linear chains in melts. Whatever the correct mechanism might be for linear chain melts, it must lead to an $M^{-a}$ dependence for the diffusion constant with $a$ in the 2.0−2.1 range, since this is the experimentally observed behavior for melts. The similarity of the dependence of $D_{cm}$ on $M$ for this melt mechanism and the reptation prediction for $D_{cm}$ is sufficient to explain the agreement of the diffusion constant for linear chains in melts and microgels. Furthermore, it is clear from theoretical studies[8-17] and from experimental data[18] on systems with various topologies that this $M^{-2}$ to $M^{-2.1}$ dependence of $D_{cm}$ is not unique to the reptation mechanism. Consequently, there is no difficulty in reconciling the diffusion data for linear chains in microgels with a nonreptation mechanism for the motion of linear chains in melts.

**Acknowledgment.** This work is supported by NSF Grant CHE-9422786. The author also gratefully acknowledges support from the Center for Photoinduced Processes funded by the National Science Foundation and the Louisiana Board of Regents.

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MA960229S