

On the dynamics of large ring polymers in the melt - a SANS, neutron spin echo and PFG - NMR study

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Abstract

The non-crossing requirement in non-concatenated ring polymers creates topological constraints, which impose important restrictions on the phase space of the system. For ring polymers interpenetration is costly entropically and compact structures evolve for high molecular weights - ring polymers are assumed to become mass fractals confining rings into territories. Other than the dynamics of linear or branched chains that predominantly takes place via the chain ends, rings do not feature ends and their dynamics is considered to be self-similar and thus fundamentally different to those of chains displaying ends. The present state of the art model for the description of the internal relaxations in dense ring systems was developed by Rubinstein et al. /1/. This self-consistent Fractal Loopy Globule (FLG) model is based on the conjecture that the overlap criterion /2,3/ in the packing model for entanglements also governs the rule for overlapping loops in polymer rings. The constant overlap of loops is conjectured to occur in a self-similar way over a wide range of length scales from the elementary loop size N_e up to ring size R . The dynamics of such rings in a melt is governed by topological constraints that dilute with progressing time, because with time loops of increasing sizes are relaxed and cease to be obstacles.

Recently, combining results of SANS /4/ with PFG- NMR and NSE the unique topology driven self-similar internal ring dynamics predicted by the FLG model could be verified experimentally /5/: We find the center of mass diffusion taking place in three dynamic regimes from short to long times: (i) a strongly sub-diffusive regime, where the center-of-mass mean square displacement scales as t^α ($0.4 \leq \alpha \leq 0.6$), until it reaches roughly the value R_g^2 ; (ii) a second regime with a $t^{0.75}$ scaling that (iii) at roughly $2.5 R_g^2$ crosses over to Fickian diffusion. While the second anomalous diffusion regime has been found in simulations and was predicted by theory, we attribute the first one to the effect of cooperative dynamics resulting from the correlation hole potential. The internal dynamics at scales below the elementary loop size is well described by ring Rouse motion. At larger scales the dynamics is self-similar and follows very well the predictions of the scaling models with preference for the FLG model.

References

References:

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