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EXPERIMENTAL TESTS OF POLYMER REPTATION

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Michal Komlosh

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ABSTRACT

Pulsed Gradient Spin Echo Nuclear Magnetic Resonance (PGSE-NMR) and rheology measurements were used to test whether the dynamics of entangled polymer chains in semidilute solution follow the reptation theory. Nine molar masses from 1 to 20 million daltons at a fixed concentration of 4.96% w/v along with a range of concentrations from 4.96% to 23.58% w/v at fixed molar mass of 3 million daltons were studied using PGSE-NMR techniques. The response to mechanical deformation of five different concentrations from 4.96% to 23.58% w/v at fixed molar mass of 3.9 million daltons was also studied. The distance and time scales accessed by PGSE-NMR were 20 to 1000 nm and 10 to 3000 ms respectively. As a result the mean square segmental motion over three reptation regimes was obtained and the reptation fingerprint, $\langle (r(t) - r(0))^2 \rangle \sim t^{1/4}$, was observed. The resulting concentration and molecular weight scaling laws for the tube disengagement time, center of mass diffusion and the tube diameter, which were obtained in PGSE-NMR and rheology experiments, were found to be in good agreement with the reptation theory and its standard modifications, and a good quantitative fit to the mean square displacement was given by this theory.

Local anisotropic motion of polymer chains at the level of the Rouse time was observed using double-PGSE NMR methods. These suggested a possible cooperative motion of polymer chains in entangled environment which challenges the basic assumptions of the reptation theory.

Evidence of intra-chain spin diffusion was found. As a consequence relevant corrections incorporating the phenomenon into the PGSE-NMR data had to be made.

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CONTENTS

Abstract	i
Acknowledgments	ii
1. Introduction	1
2. Theoretical models of Polymer dynamics	4
2.1 Rouse model	4
2.2 The Reptation model	9
2.3 Rheology	14
2.4 Concentration dependence	22
2.5 Modification of the Reptation theory	27
2.5.1 Contour length fluctuations	28
2.5.2 Double reptation	30
2.5.3 Reptons	31
2.5.4 Constraint release	33
2.5.5 Reptation and contour length fluctuations	36
2.6 Polymer-mode-coupling	37
3. Basic theory of NMR	41
3.1 Semi-classical description of NMR	41
3.1.1 The rotating frame	42
3.1.2 rf pulse	43
3.1.3 Detection	44
3.1.4 Spin- lattice and spin-spin relaxation process	44
3.2 Spin echo and stimulated echo experiments	46
3.3 Translational motion of spins	47
3.3.1 Diffusion measurement in the presence of continuous magnetic field gradient.	47
3.3.2 Pulsed Gradient Spin Echo experiment	51
3.3.3 Double PGSE	53
3.3.4. Stabilization of the echo	54

4. Instrumentation	57
4.1 The features of the NMR instrument	57
4.2 Data acquisition and processing	57
4.3 The gradient coil	58
4.4 Power supply	61
4.5. Dual gradient apparatus	62
4.6. Disaster, safety and other aspects	63
4.6.1 Safety fuses	64
4.6.2 Resistors box	64
4.6.3 Screened cables	64
5. NMR results	65
5.1 Materials and methods	65
5.2 Fitting the tube/reptation model	66
5.3 Concentration dependence	68
5.4 Discussion	68
6. Rheology results	72
6.1 Materials and methods	72
6.2 Results	73
6.3 Discussion	74
7. Spin diffusion	77
7.1 The dipolar interaction	77
7.2 Spin diffusion	79
7.3 Direct measurement of Spin Diffusion	81
7.4 Results	87
7.5 Discussion	87
8. Anisotropy of segmental motion	90
8.1 Double-PGSE signal attenuation for the reptation model	90
8.1.1 Local one dimensional motion	91
8.1.2 Locally anisotropic motion model (constant anisotropy)	92
8.1.3 Locally anisotropic motion model (changing anisotropy)	93
8.2 Materials, methods and results	94
8.2.1 Instrumentation test	95

8.2.2 Reference system	95
8.2.3 Polymer system	96
8.3 Discussion	97
9. Summary & future work	99
9.1 Summary	99
9.2 Suggestions for future work	100
Bibliography	102
Appendix	107