NMR measurement of polymer alignment under deformational flow

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Overview

The nuclear spin Hamiltonian and orientation
Deformed elastomers
Entangled polymer deformation
Imaging and velocimetry by NMR
Alignment tensor for PDMS melts
Transitions for nematic polymers in extensional flow
the nuclear spin environment

\[ H_i = -\gamma B_0 I_i z - \gamma \delta B_0 I_i z - J_i, I_i - I_i, Q I_i - \sum_{j} I_j, D I_i \]

Zeeman interaction with polarizing field
\~100s MHz

NMR and the nuclear spin environment

\[ \omega = \gamma B_0 \]
Larmor frequency

\[ \text{FT yields spectrum} \]
\[ \omega = \gamma B_0 + \mathbf{G.r} \]

\[ \mathbf{G} = |\mathbf{B}_0| \]
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\[ q = \lambda^{-1} \]

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$q = \lambda^{-1}$

$E(q,\Delta) = \exp(i2\pi qZ(\Delta))$

$q = \lambda^{-1}$
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1H NMR spectrum of ethanol

Zeeman interaction with polarizing field
~100s MHz

chemical shift (electron shielding)
a few ppm ~kHz

scalar spin-spin coupling (electron mediated)
~10 Hz

Molecular structure

ith spin Hamiltonian

\[ H_i = -\gamma B_0 I_{iz} - \gamma \delta B_0 I_{iz} - J_{ij} I_i - Q^{-1} I_i - \sum_j D_{ij} I_j \]
Molecular organisation and dynamics

\[ H_i = -\gamma B_0 I_i z - \gamma \delta B_0 I_i z - J I_i I_{ij} - \sum I_j D I_i \]

ith spin Hamiltonian

Spin interactions and orientation
dipolar coupling and quadrupolar coupling

\[ \text{quadrupole interaction (I>1/2)} \]
\[ (\text{efg from electron orbital)} \]
\[ \sim \text{Hz to } 100 \text{ kHz} \]

orientation dependence \( P_2(\cos\theta) \)

\[ \text{inter-nuclear dipolar interaction} \]
\[ \sim \text{Hz to } 100 \text{ kHz} \]

\(< P_2 > \quad \Rightarrow \text{order parameters} \]
\[ P_2(\cos\theta(r)) \Rightarrow \text{relaxation, molecular dynamics} \]
**Electric quadrupole interactions and molecular orientation**

- Principal frame: $V = \begin{bmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{bmatrix}$

- $H_Q \ll H_{magnetic}$ hence $H_Q = I V^{Diag.} I$

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- $\Delta \omega = V_{zz} P_2(\cos \theta)$ for uniaxial EFG tensor

**Deformed elastomers**

- Stretch: $\lambda_x \lambda_y \lambda_z = 1$
- Volume conserving: $\lambda_z = \lambda = L / L_0$

- $R' = \lambda R$
- $\lambda$: deformation tensor
Deuterated probe molecule in deformed elastomer

\[ \lambda, \lambda_x, \lambda_z = 1 \]

volume conserving stretch \( \lambda_z = \lambda = L/L_0 \)

\( R' = \lambda R \)

\( \lambda \) deformation tensor

"inherited" residual order "pseudo-nematic" interaction

\[ \Delta \omega \sim [\lambda^2 - \lambda^{-1}] \]

"Elastic Band" Compression Data

frequency (Hz)
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Deuteron quadrupole splitting:
\[ \Delta \omega = \omega_0 \frac{R^2}{R_0^2} P_2(\cos \theta) \]
\[ \Delta \omega = \omega_0 \frac{R'^2}{R_0'^2} P_2(\cos \theta') \]

Phantom gaussian chain, affine deformation model.

Uniaxial deformation:
\[ \lambda \]
\[ \frac{1}{\lambda} \]

Biaxial deformation:
\[ \lambda \]
\[ \lambda^{-1/2} \]
\[ \lambda^{-1} \]
Rotation w.r.t. magnetic field

principal axis of deformation

\[ c = \cos \Theta \]
\[ s = \sin \Theta \]

uniaxial deformation

\[ \langle \omega \rangle = \omega_0 \frac{1}{3} \left[ \frac{1}{2} c^2 \lambda^2 - \frac{1}{2} s^2 \lambda^2 \right] \]

bi-axial deformation

\[ \langle \omega \rangle = \omega_0 \frac{1}{3} \left[ -\frac{1}{2} \left( c^2 + s^2 \right) \lambda^2 - \frac{1}{2} c^2 \lambda^2 - \frac{1}{2} s^2 \lambda^2 \right] \]

Angular and strain effects separable

phantom gaussian chain, affine deformation model

Rotation about squeeze axis

Angular and strain effects non-separable

linear entangled polymer melts deformation under shear
alignment tensor

\[ S_{\alpha\beta} = \langle u_\alpha u_\beta - \delta_{\alpha\beta}/3 \rangle \]

\[ S_{xx} = \langle u_x^2 - 1/3 \rangle \]

\[ S_{xy} = \langle u_x u_y \rangle \]

\[ S_{\alpha\beta}(t) = \mathcal{N}_0^{-1} \sum_{n} \langle u_\alpha(n,t)u_\beta(n,t) - \delta_{\alpha\beta}/3 \rangle \]

\[ \sigma_{\alpha\beta}(t) = G_e S_{\alpha\beta}(t) \]

in steady state shear

\[ \sigma_{\alpha\beta} = G_e Q_{\alpha\beta} (\dot{\gamma} \tau_d) \quad \text{Doi-Edwards (1978)} \]
Dol–Edwards predictions for entangled polymer

accessing the full deformation tensor

alignment tensor

\[ S_{\alpha\beta} = \langle u_\alpha u_\beta - \delta_{\alpha\beta}/3 \rangle \]

\[ S_{xx} = \langle u_x^2 - 1/3 \rangle \]

\[ S_{xy} = \langle u_x u_y \rangle \]
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**Alignment Tensor**

\[ S_{\alpha\beta} = \langle u_\alpha u_\beta - \delta_{\alpha\beta}/3 \rangle \]

\[ S_{xx} = \langle u_x^2 - 1/3 \rangle \]

\[ S_{xy} = \langle u_x u_y \rangle \]

**Measurement Frame**

**Hydrodynamic Frame**

**Selecting the Required Alignment:**

Vorticity, or gradient/velocity along \( B_0 \)

Polydimethylsiloxane-650 kD

(-65 entanglements)

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Selective destruction - Spatially selective 2H spectroscopy in the evolution domain: \textit{d}-benzene in sheared PDMS

obtaining $S_{xx}$

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\[
S_{\text{zeeman}}(\theta) = S_{xx}\cos^2\theta - 2S_{xy}\sin\theta \cos\theta + S_{yy}\sin^2\theta
\]

\[
S_{xy} = \frac{1}{2}S_{\text{zeeman}}(0) + \frac{1}{2}S_{\text{zeeman}}(\pi/2) - S_{\text{zeeman}}(\pi/4)
\]

**Rheo-NMR: alignment tensor vs shear rate**

**Doi-Edwards**

$S_{xx}$, $S_{xy}$, $S_{yy}$

$\tau_d = 215$ ms

$De = 1$

**Corrner, Kilfoil and C, Physical Review E 6405, 1809 (2001)**
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Molecular weight dependence

lower M

above 800 kD observe slip

slip causes strain rate plateau for $De >> 1$
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Molecular weight dependence

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Molecular weight dependence

\[ \tau_d \sim M^{3.5} \]

using measured strain rates

Second normal stress difference

Steric hindrance in probe molecules: inherited order

polymer chain undergoing rapid segmental motions

probe molecule

free rotation

Steric hindrance in probe molecules: inherited order

polymer chain undergoing rapid segmental motions

sterically hindered rotation near polymer chain

free rotation

probe molecule

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Transforming between reference frames

matrix or hydrodynamic frame

polymer chain undergoing rapid segmental motions

molecular frame

Extensional flow in a four roll mill

selective excitation of stagnation region of extensional strain

velocity $v_y$
Extensional flow in a four roll mill

selective excitation of stagnation region of extensional strain

proton density image

image after double orthogonal selective storage

Transition in extensional flow

competition between magnetic and extensional alignment

director transition

$|\dot{\varepsilon}| > \chi_0 B_0^2 / (\mu_1 \mu_3 + \mu_2)$

magnetic susceptibility
anisotropy
Leslie viscosities

Freederickz-like transition in extensional flow

compton between magnetic and extensional alignment

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