Structure, dynamics and heterogeneity: solid-state NMR of polymers

Jeremy Titman,
School of Chemistry, University of Nottingham
Structure, dynamics and heterogeneity

Structure

* conformation, tacticity, cross linking, networks, crystallinity, polymorphism, packing effects, orientational distributions, polymer fibres and films, liquid-crystalline polymers

Dynamics

* mechanisms, rates, activation energies, mechanical relaxations, glass transition, inhomogeneous dynamics, correlation effects

Heterogeneity

* phase separation, domain sizes, polymer blends and block copolymers, morphology, semi-crystalline polymers

Hans W. Spiess
Crystallinity in PE by the $\gamma$-gauche effect

**Poly(ethylene)**

Poly(ethylene) is a semi-crystalline polymer comprising all-trans crystalline lamellae joined by conformationally disordered amorphous regions.

The carbon-13 NMR spectrum shows a narrow peak at 33 ppm and a broader one at 30 ppm.

- The broader peak can be assigned to the more disordered and mobile amorphous regions. The lower chemical shift arises from the larger number of gauche conformations present in these regions (the $\gamma$-gauche effect).

- The narrow peak can be ascribed to the more rigid crystalline regions.
**Manufacturing Conditions**

The carbon-13 NMR spectrum of poly(ethylene) reveals information about the effect of manufacturing conditions on structure.

Gel-spun ultra-high molecular weight poly(ethylene) is highly crystalline and shows a weak amorphous contribution compared to the more traditional melt-spun poly(ethylene).

Note that gel-spun poly(ethylene) shows a new crystalline phase which gives a carbon-13 line at 35 ppm.
Polymer dynamics by solid-state NMR

Most methods (dynamic mechanical spectroscopy, differential scanning calorimetry etc.) used to characterize motions in polymers merely give an indication of the timescale; solid-state NMR provides additional information about geometry, amplitude and chemical location across 14 orders of magnitude in correlation time.

**Spin-lattice Relaxation.** The observation of the minimum in $T_1$ indicates the occurrence of motions in the MHz frequency range ($\tau_c < 1 \mu s$).

**Lineshape Analysis.** The observation of motional narrowing gives information about motions in the kHz range ($\tau_c < 1 \text{ ms}$), as well as information about the geometry of motions.

**Two-dimensional NMR.** Exchange cross peaks indicate very slow motions ($\tau_c > 10 \text{ ms}$) and give detailed geometric information.
The changes in mechanical strength which occur as temperature is increased arise from the activation of different molecular motions.

- **The glass transition** generally arises when large amplitude co-operative motions of main chain segments are activated leading to a large drop in mechanical strength. High cross link densities impede the glass transition in elastomers.

- **Mechanical relaxations** at lower temperatures arise when local motions, often involving side chains, are activated. These motions give thermoplastic polymers impact strength.
Poly(tetrafluoroethylene)

PTFE is a semi-crystalline thermoplastic with

- a melting temperature for the crystalline domains around 600 K
- a glass transition temperature for the amorphous matrix around 400 K.
- several mechanical relaxations below the glass transition temperature.

Two contributions to the fluorine-19 spin-lattice and spin-spin relaxation can be isolated, originating in the crystalline and amorphous parts of the polymer respectively.
**Amorphous regions**

The amorphous \( T_2 \) increases rapidly above 220 K, while the amorphous \( T_1 \) has a minimum at 273 K. This indicates the onset of molecular motion in the amorphous regions.

* 220 K \( \tau_c \sim 20 \mu s \). \( 1/\tau_c \) must be of the order of the fluorine-19 linewidth to cause motional narrowing.

* 273 K \( \tau_c \sim 3 \) ns. \( 1/\tau_c \) must be equal to the Larmor frequency (30 MHz in this case) at the \( T_1 \) minimum.

This motion occurs at too low a temperature to be ascribed to the glass transition.

**Crystalline regions**

Both the crystalline relaxation times show a discontinuity at 292 K. This indicates a phase change in the crystalline regions.

The crystalline \( T_2 \) increases rapidly above 340 K, while the crystalline \( T_1 \) has a minimum at 450 K.

This indicates another motion starts in the crystalline regions below 340 K with \( \tau_c \sim 3 \) ns at 450 K.
Glass transition in PMMA-d5 by lineshape analysis

**Poly(methylmethacrylate)** is an amorphous thermoplastic polymer with a glass transition temperature of 398 K.

The $^2$H lineshape is a sensitive probe of motion because of the large angular resolution which arises from the broad Pake powder pattern.

- Below the glass transition (380 K) the $^2$H spectrum of backbone labelled PMMA-d5 consists of two patterns arising from the (rigid) methylene and (rotating) methyl groups.
- Above the glass transition (430 K), the methyl group shows a lineshape which is characteristic of a motion with a broad distribution of reorientation angles and correlation times.
- At high temperatures (450 K), the signal consists of a slightly broadened isotropic line, characteristic of the fast motion limit ($\tau_c \sim 1 \, \mu$s).

Slow dynamics by exchange NMR

During the mixing period of the two-dimensional exchange experiment molecules exchange orientations due to molecular motion.

* For a **random jump motion** with $\tau_c$ shorter than the mixing time a complete redistribution of intensity away from the diagonal occurs.

* For a **well-defined jump angle** intensity is redistributed into an elliptical ridge, the shape of which is determined by the geometry of the motion.
**Poly(oxymethylene)** is a semi-crystalline thermoplastic with a highly mobile amorphous matrix with a glass transition temperature of 200 K. The crystals form helical structures in which 9 monomers occupy 5 turns of the helix. This implies that adjacent CH₂ groups along the helix are related by a 200° rotation.

**Experiment**

**Simulation**
**252 K**: two-dimensional exchange spectra with mixing times of up to 4 s show only diagonal intensity, indicating that any motions in the crystalline parts are slow on a timescale of 4 s.

**335 K and 360 K**: two-dimensional exchange spectra with mixing times above 1 s show elliptical ridges. These can be assigned to jumps of 200°, 400° and 600° respectively.

Hence the crystalline regions of poly(oxymethylene) have a well-defined jump motion with \( \tau_c \sim 1 \text{s} \) which corresponds to a translation of the polymer chain.
**Poly(ethylmethacrylate)** is an amorphous thermoplastic polymer with a glass transition temperature of 338 K. The sample is 20 % enriched with carbon-13 at the carboxyl group, allowing investigation of the side-group motion through analysis of the lineshape of the carboxyl carbon.

**At 295 K:** the spectrum shows a powder pattern with principal components \( \nu_{11} = 268 \text{ ppm}, \nu_{22} = 150 \text{ ppm}, \nu_{33} = 113 \text{ ppm.} \)

**Above \( T_g \):** lineshape changes indicate large-amplitude motions with rates exceeding 10 kHz, the width of the powder spectrum.

**At 395 K:** anisotropic chain motion leads to a motionally averaged axially symmetric tensor. This suggests that the \( \nu_{33} \) axis remains invariant during the motion which could result from either a rotation about this axis or by \( \pi \) flips of the side group.
**Exchange NMR**

The exchange signal at $\nu_{33}$ is low compared to that between $\nu_{22}$ and $\nu_{11}$.

The exchange pattern can only be explained by assuming that $\pi$ flips of the side group are accompanied by a rotation about the main chain.

**Simulation**

The simulated spectrum was calculated for a rocking amplitude of $\pm 20^\circ$ coupled to the $\pi$ flips and assuming that only 40% of the segments participate in the motion. This is indicative of a heterogeneous distribution of correlation times.

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**At 355 K**: 17 K above $T_g$ 85% of the side groups take part in the motion, leaving 15% trapped in their local environments due to their bulky size. The motion involves a rocking amplitude of ±40° coupled to the $\pi$ flips.

Hence, for PEMA even above $T_g$ the molecular motion is anisotropic, with molecular geometry similar to that in the glass.

**At 365 K**: 27 K above $T_g$ the motion involves a rocking amplitude of ±50° coupled to the $\pi$ flips and all segments participate in the motion.
Main chain dynamics in PEMA by $^2$H exchange NMR

**PEMA-d$_5$**

* This sample is enriched with deuterium, allowing investigation of the main-chain motion through analysis of the $^2$H exchange NMR spectrum.

* The spreading of exchange intensity with mixing time indicates increasing reorientation angles, suggesting planar rotational diffusion of main chain segments around the local chain axis.

* The equilibrium positions of the backbone rocking motions become increasingly imprecise after a large number of side chain flips, resulting in a slow rotation of the main chain itself.

* The simulations involve planar rotational diffusion with $\tau_c = 600$ ms.

Coupling of $\alpha$- and $\beta$-relaxations in PEMA

* **Dielectric relaxation measurements** detect the changes of the electric dipole moment caused by dynamics of the carboxyl side group and are therefore sensitive to the $\beta$-relaxation, as is $^{13}$C NMR of the carboxyl carbon.

* **Photon correlation spectroscopy** is sensitive to main chain fluctuations and shows an almost temperature independent $\alpha$-process with a distribution parameter $\beta_{KWW} = 0.35$, equivalent to a distribution of $\tau_c$ approximately 3 decades wide.
Dynamics in complex systems by MAS exchange NMR

Poly(styrene)-poly(vinylmethylether) blends

* The 50/50 PS-PVME mixture cast from toluene shows a single proton spin-lattice relaxation time which has a temperature variation intermediate between that for the pure components. This indicates that this blend is homogeneous down to a length scale of 20 nm.

* The 50/50 mixture cast from chloroform shows two separate proton spin-lattice relaxation times which have a temperature variation similar to that for the individual components. This indicates that the blend has phase separated into regions of poly(styrene)-rich and poly(vinyl methyl ether) rich material.
There are three periods in a typical spin diffusion experiment:

* **Selection** of the magnetization from a part of a heterogeneous sample, using differences in mobility or chemical shift.

* During a **mixing time** spin diffusion down the resulting magnetization gradient redistributes the magnetization.

* **Detection** of the redistributed magnetization to probe the spin diffusion.

The rate of the observed spin diffusion can be related to the **morphology** of the heterogeneous sample and the **sizes** of the phase domains.
Miscibility in PS-PVME blends by direct observation

* The 50/50 PS-PVME mixture cast from **chloroform** shows cross peaks between PS protons and between PVME protons. This indicates that this blend is phase separated.

* The 50/50 mixture cast from **toluene** shows cross peaks between PS and PVME protons. This indicates that the blend is homogeneous.

* The spin diffusion rate and hence the domain size can be extracted from the cross peak build-up.
Lamellae thicknesses in PS-PMMA block copolymers

This experiment involves:

* PMMA block methyl proton selection according to chemical shift
* spin diffusion which redistributes magnetization to the PS blocks
* carbon-13 detection after TOSS for spectral simplification

Note the increase in PS phenyl carbon intensity at longer mixing times.

The equal lengths of both blocks in the symmetric copolymers ensures a lamellar structure which makes the quantitative analysis straightforward.

The spin diffusion data yield domain sizes which are consistent with the scaling law $M_n^{0.66}$ where $M_n$ denotes the molar mass of the blocks.
Orientational order by rotor-synchronized MAS

With rotor-synchronized acquisition partially ordered materials result in MAS sidebands with distorted phases and amplitudes.

This can be used as the basis of a new two-dimensional experiment which separates molecular structure via the chemical shift in $\nu_2$ and a sideband pattern in $\nu_1$ which depends on the degree of orientational order.

A homologous series of poly(siloxanes) shows changes in the degree of order on the (supposedly) disordered polymer backbone as a function of flexible spacer chain length and parity.

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