



Magnetic Resonance in Porous Media 2026

Groupement
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TD-NMR in Semicrystalline Polymers: Morphology and Dynamics

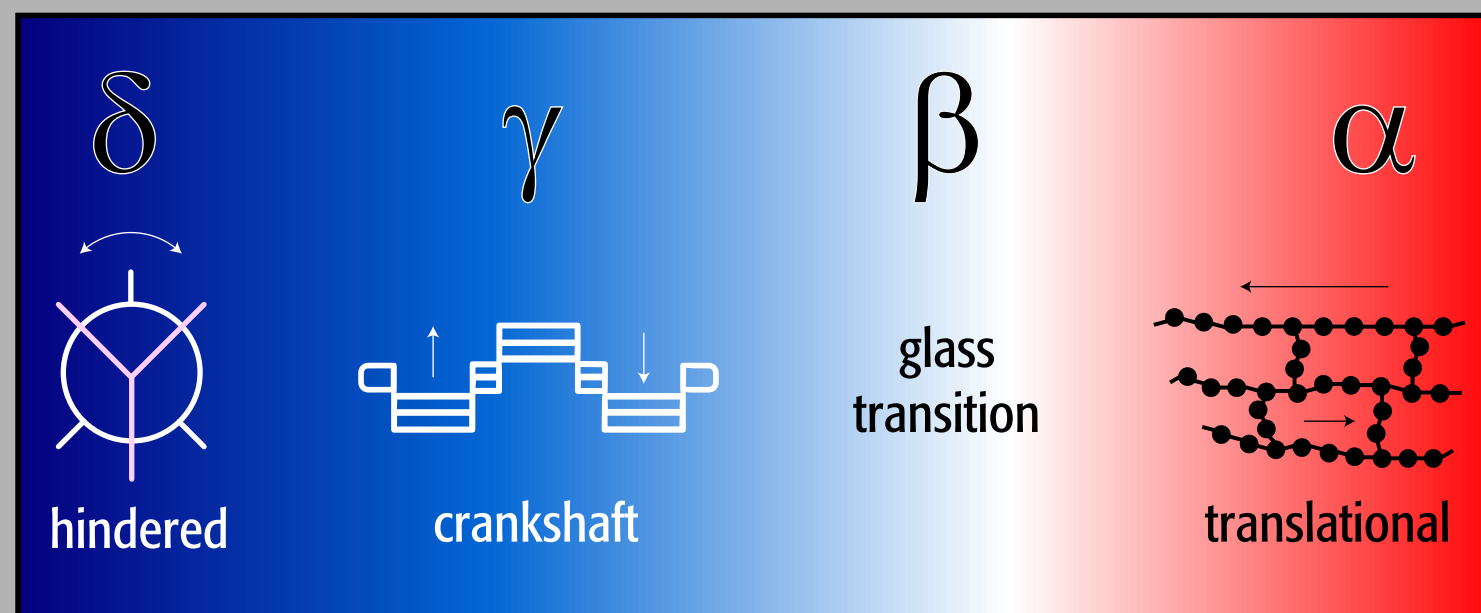
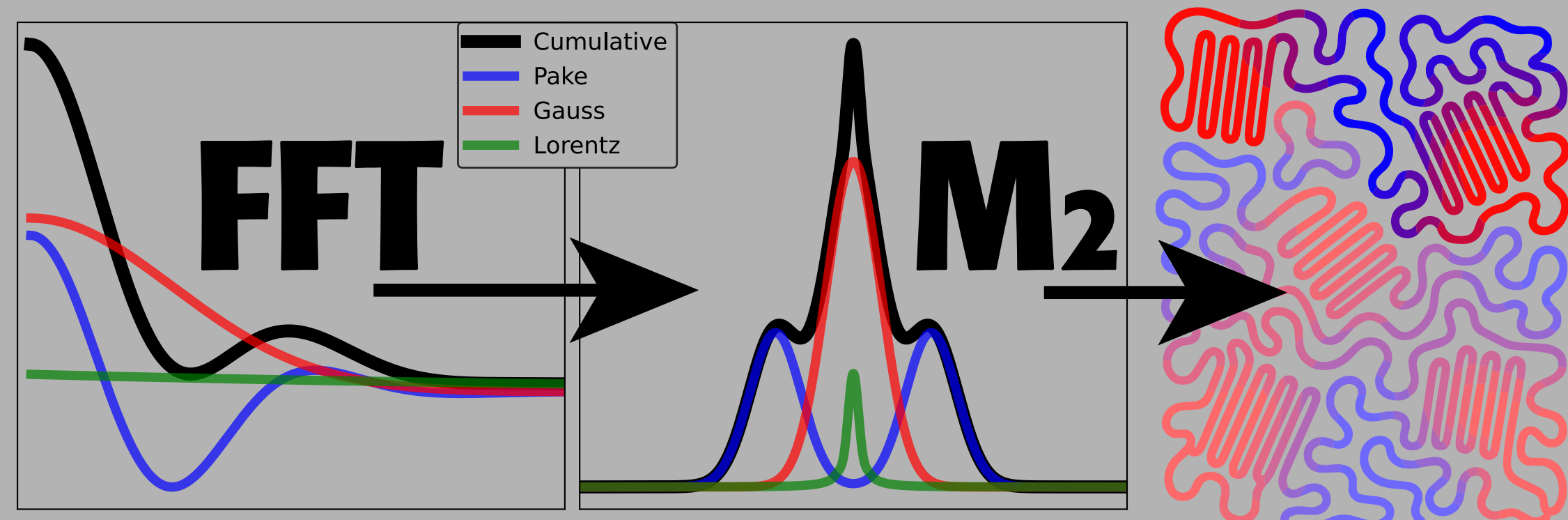
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Introduction

Polyethylene (PE) and polypropylene (PP) are widely used polymers. Despite their simple chemical structure, they have complex morphology, where crystalline, amorphous and interfacial regions closely intertwine. These regions differ in molecular mobility, which strongly influences the macroscopic properties of the material. TD-NMR is sensitive to molecular dynamics and dipolar interactions, and is useful for studying morphology. We use one of the TD-NMR analysis pathways Second-Moment Gaussian Approximation (**SMGA**), which relates the initial decay of the NMR signal to the second moment M_2 , reflecting the strength of dipolar interactions. Here, we investigate the temperature dependence of relaxation in PE and PP to characterize molecular motions and their relationship with polymer morphology.



Spin-lattice relaxation T_1 is sensitive to molecular motions occurring near the NMR observation frequency. As temperature increases, different molecular motions enter the NMR observation window, producing characteristic maxima in the relaxation rate R_1 .

Three main relaxation processes are usually distinguished in semicrystalline polymers. The α relaxation occurs at high temperatures and is associated with cooperative motions in crystalline regions. The β relaxation involves segmental motions in non-crystalline regions and is often discussed in connection with the glass transition. The γ relaxation comes from localized motions, such as crankshaft-like rotations and trans-gauche rearrangements of short chain segments.

The temperature dependence of R_1 can be described using spectral-density models. BPP assumes a single correlation time, while Cole-Davidson accounts for a distribution of correlation times.

Results

The temperature dependence of M_2 reveals changes in molecular mobility in PE and PP. In general, M_2 decreases with increasing temperature due to motional averaging of proton-proton dipolar interactions.

The plateaus in M_2 indicate regions of nearly constant motional averaging, while further decreases reflect the activation of additional molecular motions. In PE, samples with higher crystallinity generally retain stronger dipolar interactions up to higher temperatures, while PP shows a similar, but less pronounced, dependence.

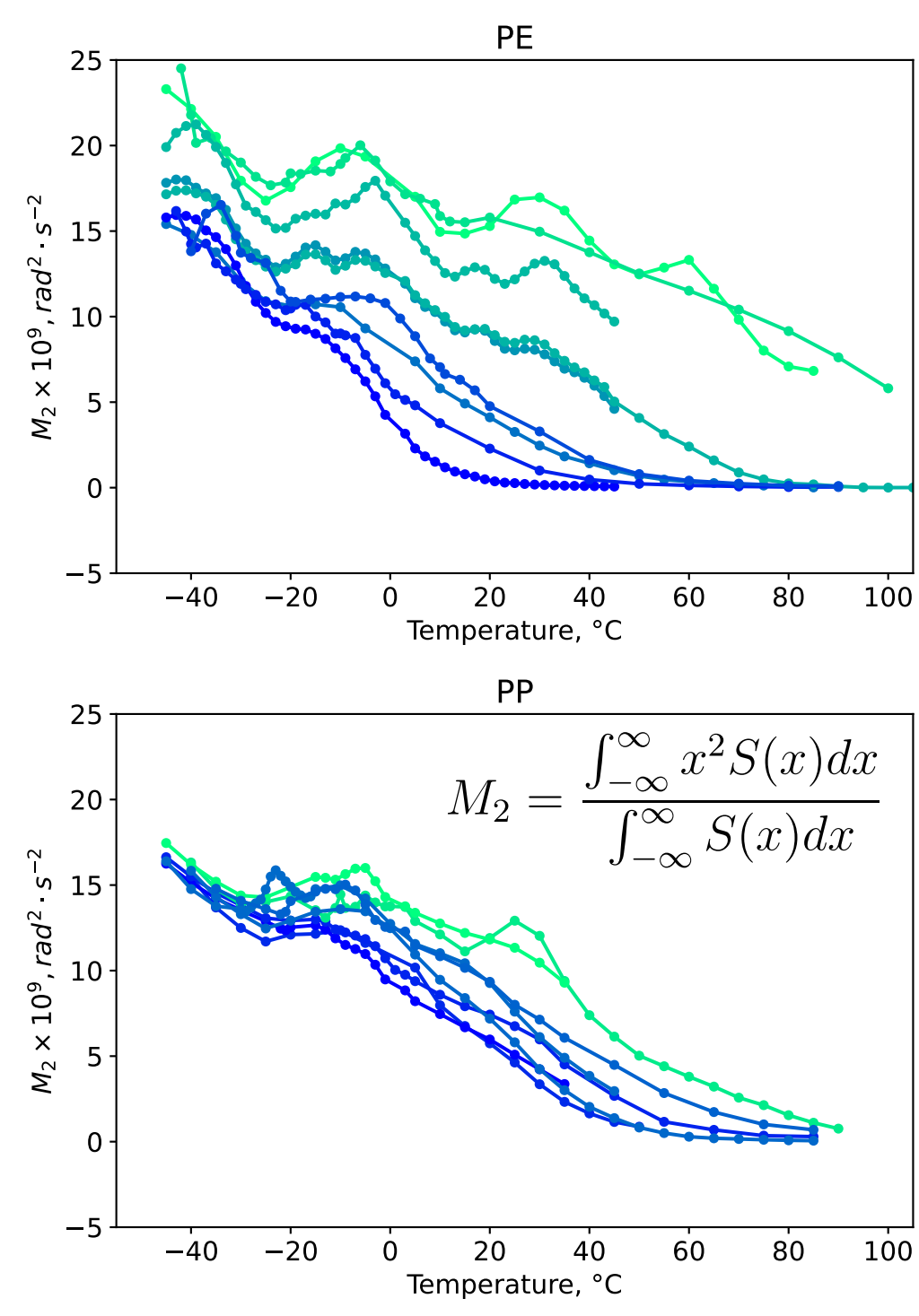


Fig. 1.1 Melting curves for PE and PP

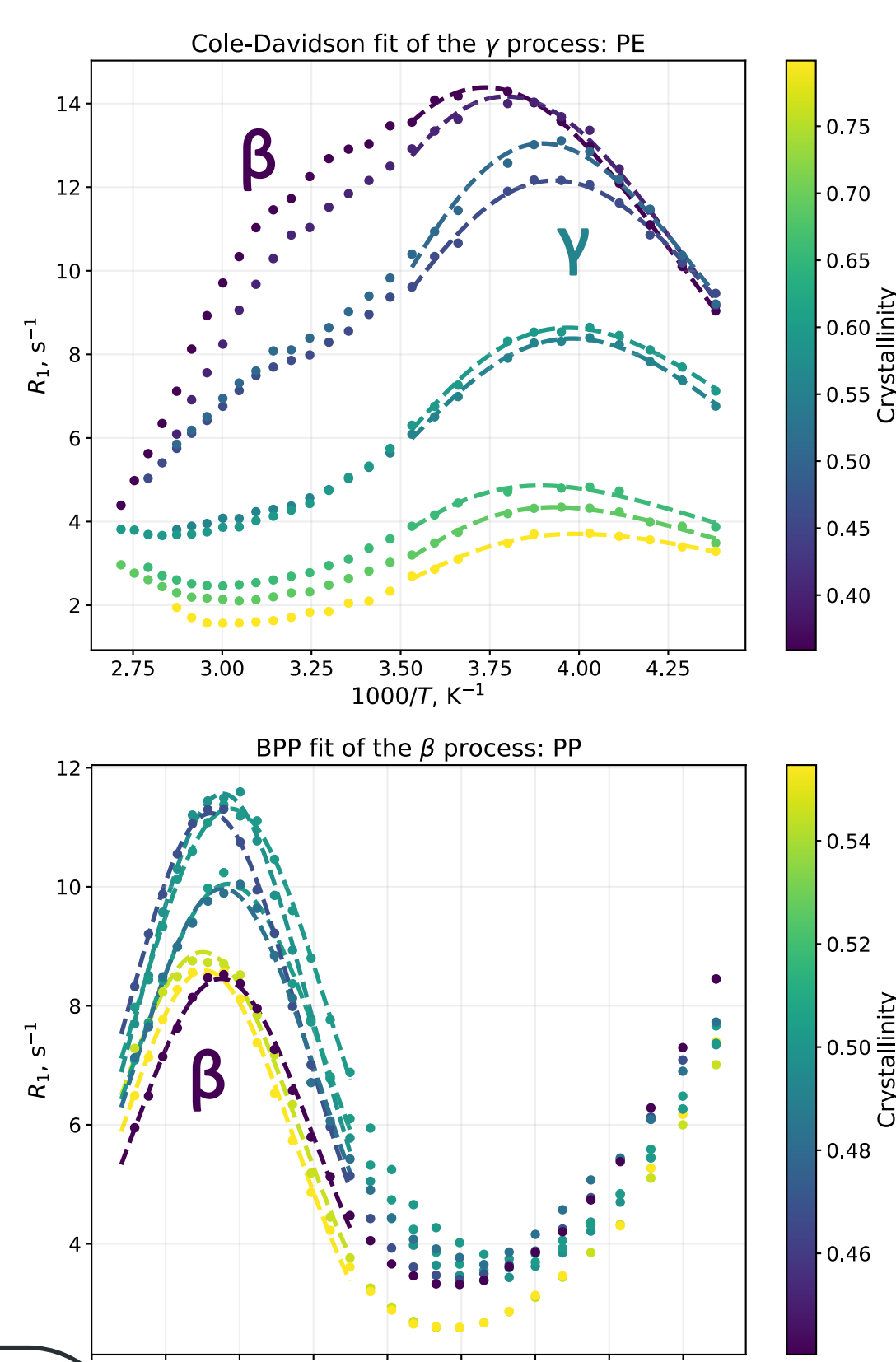


Fig. 2.1 R_1 Temperature dependence

The temperature dependence of R_1 shows distinct relaxation processes in studied polymers.

The main maximum in PE is attributed to the γ relaxation, while the pronounced maximum in PP corresponds to the β process.

For PE, the BPP model cannot describe the experimental curves equally well over the entire crystallinity range. The Cole-Davidson model gives better agreement, with β decreasing from approximately 0.7 to 0.25 as crystallinity increases. This indicates a progressively broader distribution of correlation times in more crystalline samples. For PP, the β relaxation is described reasonably well by BPP. Introducing a distribution of correlation times does not significantly improve the fit.

The activation energies calculated from the fitting, assuming Arrhenius relation, align well with literature data.

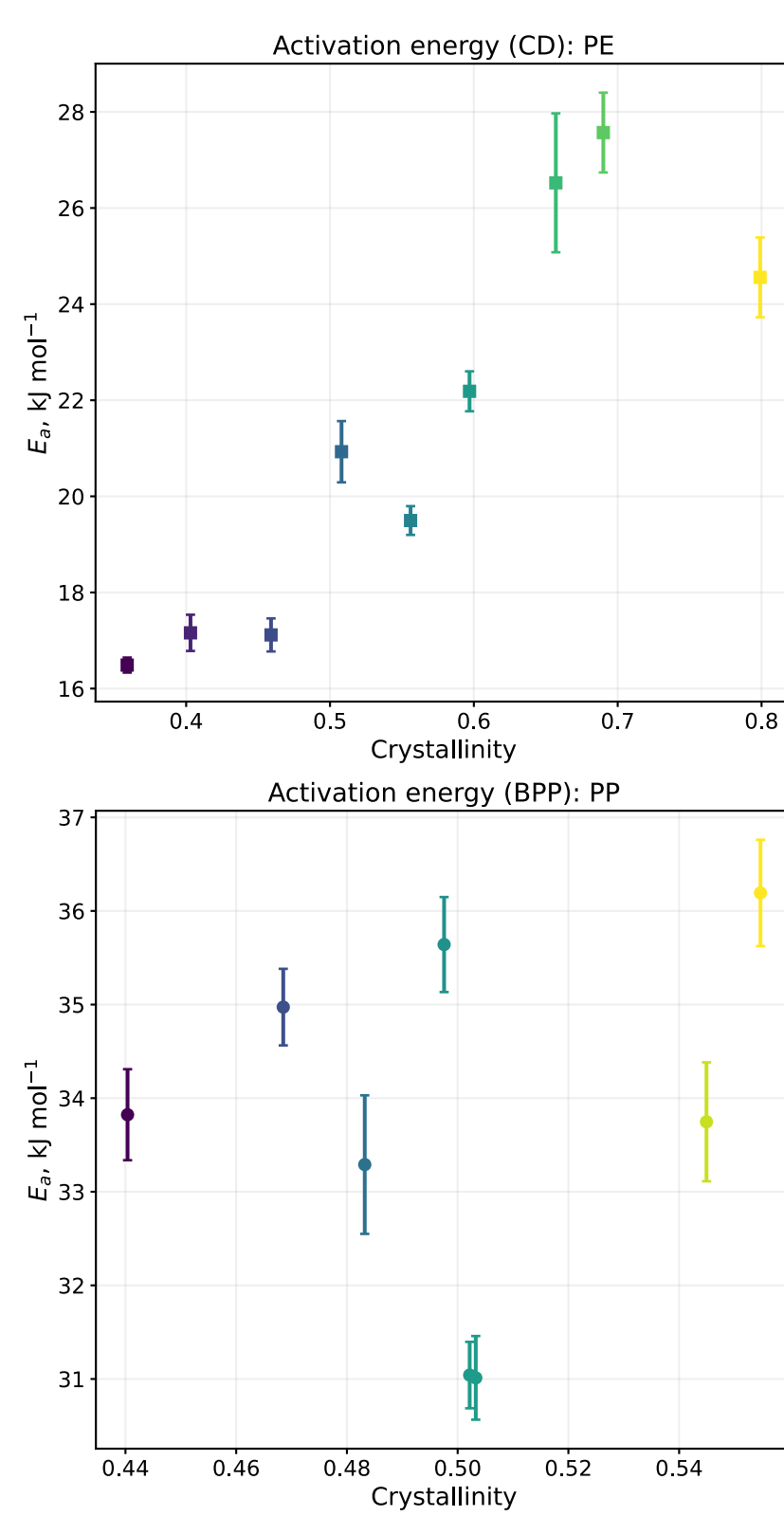


Fig. 2.2 E_{act} vs crystallinity

Fig. 3.1 Temperature-dependent T_1 distributions (ILT: 100 points, 10–2000 ms, second-order Tikhonov regularization). Round markers represent monoexponential T_1 values.

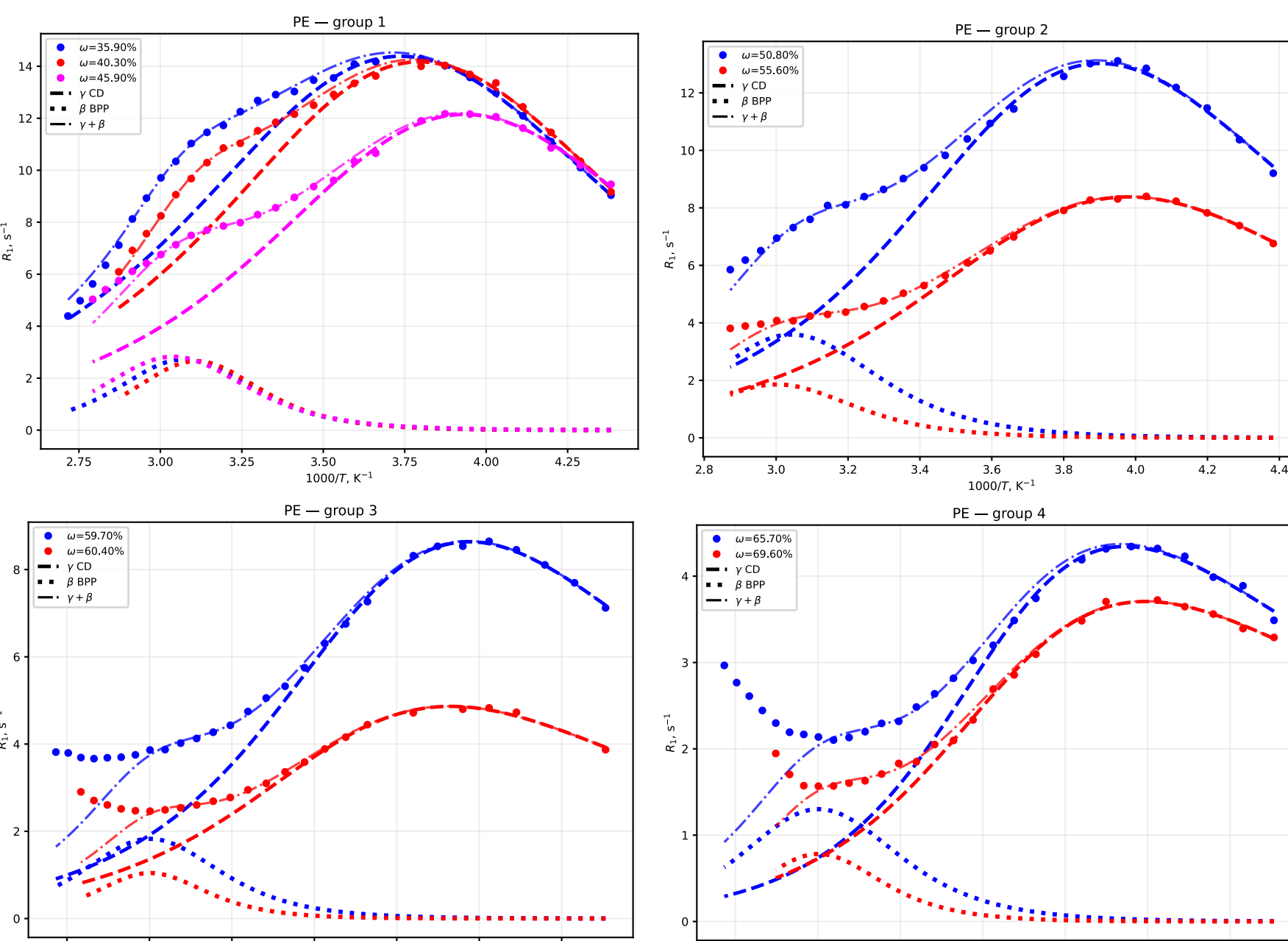
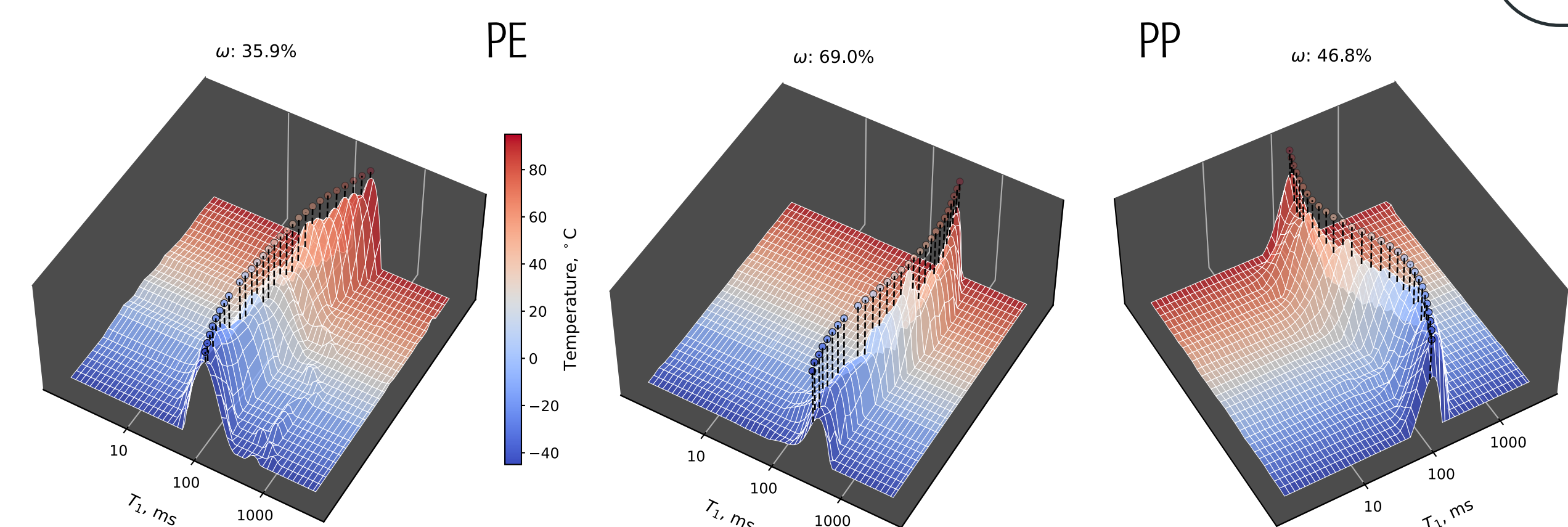


Fig. 4.2 Temperature dependence of the M_2 for PE polymer.

The ILT distributions are generally asymmetric, reflecting the wide heterogeneity. However, the relaxation curves rarely allow a reliable separation into two distinct peaks.

Pronounced asymmetry and occasional peak splitting are observed mainly at lower temperatures. With increasing temperature, the distributions shift towards shorter T_1 values as molecular motions become faster.

The positions of the main ILT peaks follow the temperature dependence obtained from monoexponential fitting. The broad distributions indicate overlapping relaxation environments rather than clearly separated contributions from individual polymer phases.

The Goldman-Shen experiment was used to estimate the dimensions of amorphous domains in PE and PP. The initial magnetization transfer was analysed as a function of the square root of diffusion time.

The spin-diffusion coefficient was calculated using M_2 obtained from DQ-filtered spectra at approximately 60 μ s, where the amorphous contribution dominates. This avoids multiparametric spectral decomposition.

The resulting domain sizes are on the nanometer scale and show good agreement with literature values.

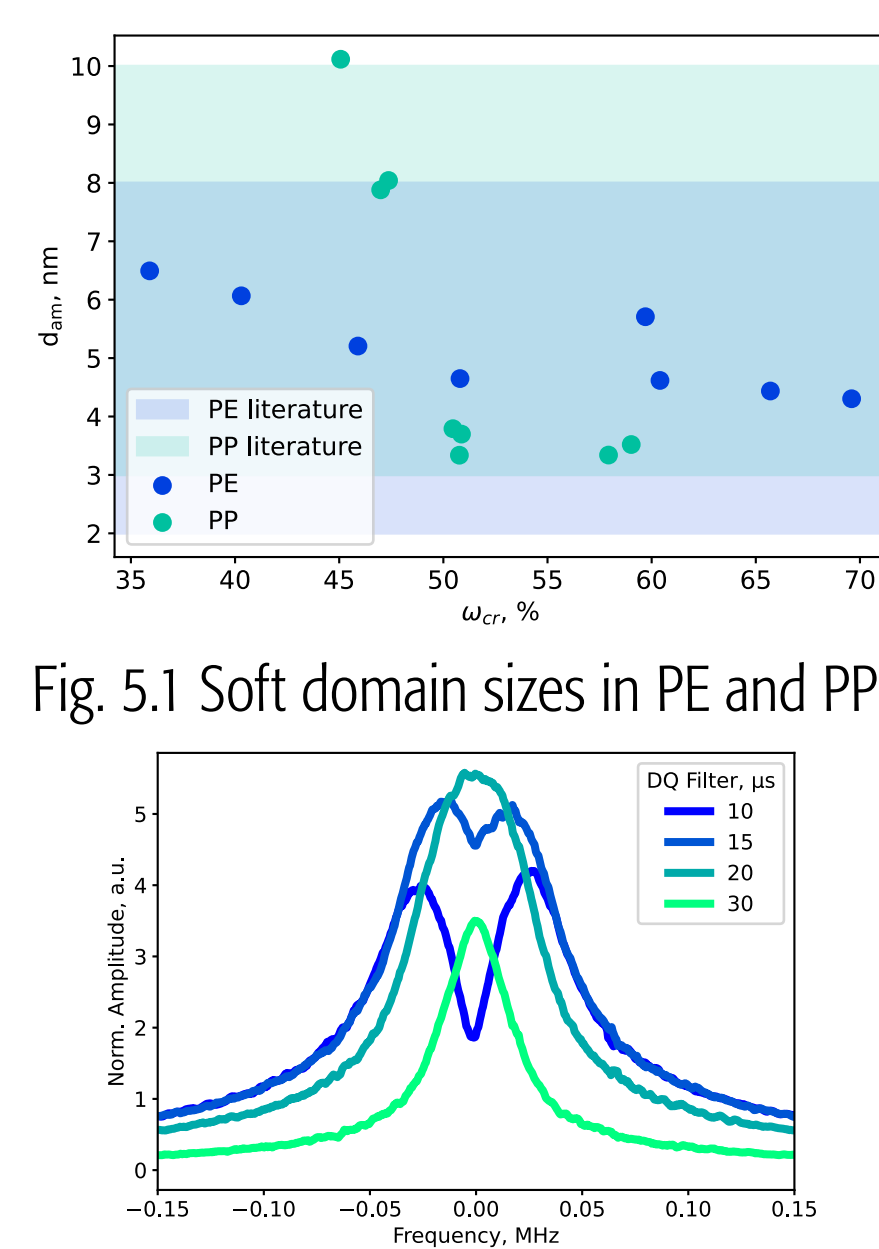


Fig. 5.1 Soft domain sizes in PE and PP

Fig. 5.2 DQ filtered NMR spectra

At higher temperatures in HDPE, an additional contribution is attributed to α relaxation. Its intensity increases with crystallinity, but the relaxation maximum remains outside the investigated temperature range.

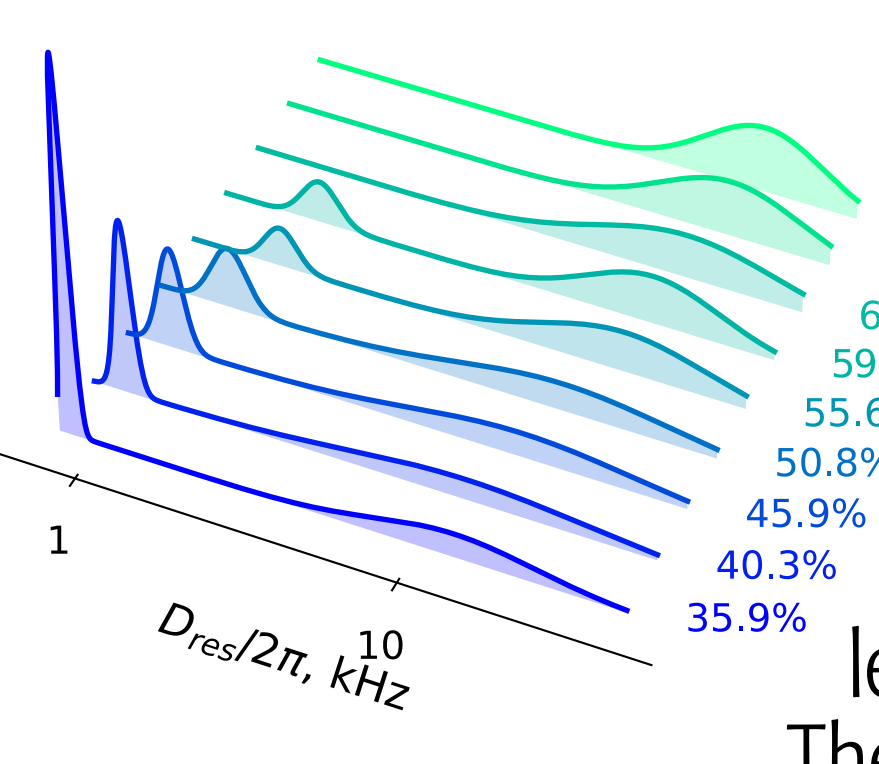


Fig. 6.1 $P(D_{res})$ for PE

The normalized DQ build-up curves were analysed to obtain distributions of residual dipolar couplings. The distributions show considerable heterogeneity of molecular mobility within the samples.

With decreasing crystallinity, the contribution of weaker dipolar couplings becomes more pronounced, reflecting an increasing fraction of less constrained chain segments.

The differences between PE and PP indicate distinct distributions of molecular constraints, even for samples with comparable crystallinity.

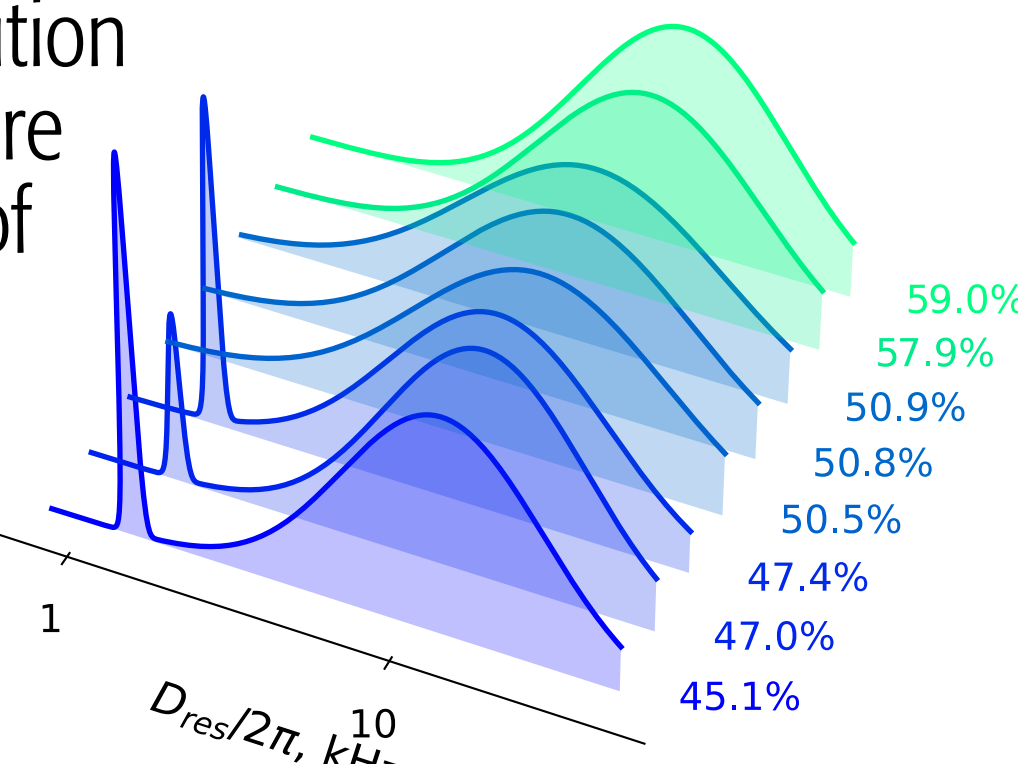


Fig. 6.2 $P(D_{res})$ for PP

Conclusions

Temperature-dependent TD-NMR measurements of PE and PP provided information on molecular mobility, phase composition and morphology.

- M_2 analysis revealed temperature-dependent changes in molecular mobility and their dependence on crystallinity.
- T_1 relaxation revealed α , β and γ processes, allowing estimation of activation energies and distributions of correlation times.
- ILT confirmed relaxation heterogeneity, although distinct components could rarely be resolved.
- DQ-MQ provided distributions of residual dipolar couplings, reflecting molecular constraints and local ordering.
- Goldman-Shen measurements yielded amorphous domain sizes on the nanometer scale, in good agreement with literature.

