Introduction: Synthetic Polymers

Synthetic polymers, with repeat unit numbers of a few tens up to millions, are chemically simpler than their biological counterparts (proteins, DNA, polysaccharides). Homopolymers ideally consist of only one and the same repeat unit (monomer), and copolymers have a few, up to maybe three or four, chemically different monomers. Nevertheless, synthetic polymers are characterized by a wide complexity in their structure and dynamics, and this article highlights the possible investigation of a variety of important aspects in this field by nuclear magnetic resonance (NMR). Complexity in synthetic polymers arises for different reasons, which shall be summarized in this section.

Generally, one can distinguish different linear and branched chain architectures, as shown in Figure 1. The different branch points in such structures are readily distinguishable by NMR, provided their concentration is high enough. However, the most important structural aspects arise more locally within the chains. First, and in contrast to most biological macromolecules, weakly hindered rotation around different bonds is usually possible, giving rise to different conformational states, and these exhibit distinct chemical shifts in many cases. For the trans and gauche conformations of a saturated alkane chain (= polyethylene) sketched in Figure 1, a $^{13}$C chemical shift difference of ca. $-5.2$ ppm arises due to the so-called $\gamma$-gauche effect, which describes changes in shielding when main- or side-chain atoms, that are separated by three bonds, come closer to each other for a specific conformation. For other substituents or compositions, the effect can be even bigger ($-7.2$ ppm for $C_0\cdots O_g$). Depending on the physical state (solutions of varying viscosity, bulk melt, or glassy state), the different conformations either interconvert rapidly, leading to the observation of a Boltzmann-weighted average chemical shift, or are fixed on the timescale defined by the inverse frequency separation, leading to the observation of distinct shifts for distinct conformations. In molten polyethylene, the $^{13}$C shift differs by $\sim 2$ ppm from the all-trans conformation; the latter being independently measurable on the crystalline phase. If the three conformations were equally populated, an average shift of $2 \times 5.2/3 = 3.5$ ppm would be expected. The lower observed shift indicates that the trans conformation is favored. The intermediate situation corresponds to the well-known scenario of chemical shift exchange and coalescence, and is characterized by broad lines. Such a line broadening may either be a valuable source of information on conformational dynamics, or can be avoided by heating or cooling, or using a more or less viscous solvent.

Second, despite their chemical regularity, local configurations may well be different, and in this regard, geometrical and positional isomerism, as well as stereoisoochemistry, plays an important role. Geometrical and
positional isomers arise when polymerizable monomers can be attached to each other in different ways, for example head-to-head versus heat-to-tail connections. This leads to distinctly different structural motifs and consequently, to meaningful differences in the NMR spectra, readily interpreted by standard rules and procedures. Depending on the specific mode of polymerization, such forms of isomerism are usually easy to control by the specific chemistry, leaving stereoisomerism as a more important structural parameter.

Stereochemical sequence analysis is thus the most frequently studied aspect in solution-state NMR of polymers, as the stereoregularity is in most cases the dominant factor that determines to which extent the polymer is semicrystalline or amorphous, with large impact on the physical properties of the material. In vinyl polymers, a stereoregular polymer is either isotactic or syndiotactic. These two tacticity patterns differ in the stereochemical diad composition (meso, m vs. racemic, r) of the main chain, as is shown in Figure 2. Importantly, polymers with extended isotactic (…mmm…) or syndiotactic (…rrr…) or syndiotactic (…rrr…) trains usually crystallize, as the regularity allows long-range ordering of the chain molecules, resulting in material with very specific properties. The tactic sequences usually form regular helices, with polyethylene as the simplest case forming a 2₁ helix (2 monomers per 360° turn), corresponding to an all-trans structure. Owing to the γ-gauche effect, valuable information on the helical structure may be attained by high-resolution 13C solid-state NMR. Atactic polymers usually do not crystallize (with poly(vinyl alcohol) as a prominent exception).

Four major factors determine the bulk properties of a polymer: the glass transition temperature ($T_g$), the tacticity, the degree of branching, and the monomer composition and distribution in the case of copolymers. Schematic structures are given in Figure 3. $T_g$ is largely determined by the chemical structure, where as a rule of thumb, more rigid (e.g., aromatic or conjugated) backbone structures lead to a higher $T_g$. Stereoirregular linear homopolymers, highly branched structures, and random copolymers do not tend to crystallize well, and may either exist as a disordered melt above $T_g$ or as a glass below $T_g$ (such as plexiglas), the difference being the segmental mobility and thus the overall dynamics. Although a polymer melt may still be able to flow (depending on the molecular weight and the degree of branching), cross-linking of the chains (Figure 3(b)) leads to a shape-persistent material that is either elastic (above $T_g$) or rigid (below $T_g$), the latter being referred to as a thermoset. Most important polymer materials are thermoplastics or thermoplastic elastomers, which flow

Figure 2  Different forms of tacticity of vinyl polymers made from a H₂C≡CAB monomer. Sequences of two or more stereocenters (diads, triads, tetrads, etc.) are referred to by their stereochemical diad succession, for example, mrrr for the specific hexad example at the bottom.

Figure 3  Schematic structures of bulk polymers. (a) Melt or glass, (b) network, that is, elastomer or thermoset, (c) semicrystalline structure, (d) phase-separated (here lamellar) di- or tri-block copolymer. Polymer melts and glasses, and elastomers and thermosets, respectively, differ in their dynamics. Although rapid segmental as well as larger-scale motion is possible in the former, dynamics in the latter are restricted to local vibrations and side-chain motions ($β$, $γ$, … subglass processes).
and can be injection-molded at high temperatures, and are either rather rigid or elastomeric and shape persistent at ambient temperature.

Generally, even perfectly stereoregular, and thus crystallizable polymers never crystallize completely due to arrested kinetics associated with the necessary large-scale topological reorganization, leaving a material with rigid crystalline lamellae interleaved with a mobile amorphous phase (see Figure 3(c)). Consequently, these polymers are thermoplastics below the crystalline melting point, $T_m$. Thermoplastic behavior can also be achieved with block copolymers, in which chemically different subchains are connected by a bond. Chemically different polymers usually do not mix, and in the case of block copolymers, which exist as di-, tri-, or multiblock structures, the phase separation length scale is limited by the size of the chemically homogeneous blocks (usually a few tens of nanometers). This leads to a rich variety of possible nano- and microstructures (see Figure 3(d)), lamellae of a symmetric di-block being one example. If one of the blocks is below $T_g$ at ambient temperature, the material is again a thermoplastic, as the rigid subphase acts as a cross-linker. From these examples, it is clear that the understanding of polymer materials requires structural and dynamic information over length scales from the molecular to the micrometer range, and dynamics from picoseconds (local vibrations) to seconds (flow, yield processes). NMR is essentially capable of covering these length and timescales, and it is thus a valuable tool providing atomic-level information that can complement many macroscopic property measurements.

In the following sections, the investigation of many of the above aspects by either solution- or solid-state NMR is addressed. The amount of literature on these subjects is vast, and while the authors have tried to cover what they consider the most important aspects, the choice of the presented topics is of course a matter of their personal preference. They have deliberately omitted pulsed gradient methods, as applied in diffusion or imaging studies of polymeric systems. Covering these fields is beyond the scope of this short contribution, and the authors refer the reader to specialized texts such as those of Kimmich and Blümich mentioned in the Further Reading section. The authors have also chosen not to cover multinuclear NMR using for instance $^{29}$Si, $^{15}$N, $^{31}$P, and many other quadrupolar nuclei, which play an important role in the study of inorganic and functional polymers. It should be clear that the principles to be discussed here in relation to $^1$H and $^13$C NMR of small molecules may directly be applied to polymers, provided that a suitable solvent exists. Often, it is in fact not easy to prepare a polymer solution of sufficiently low viscosity, which is necessary to ensure rapid tumbling of the polymer coils as well as fast averaging over the different conformational states. Otherwise, broad lines or, for the case of fixed conformations, complex multiplet signals can challenge the interpretation of the spectra. In particular, solutions of high-molecular-weight polymers may be very viscous even under high dilution, requiring significant reductions of the concentration. Often, when the solvent is thermodynamically poor, the polymer tends to aggregate, again causing a broadening of the lines. Not uncommonly yet counterintuitively, the thermodynamic quality of a solvent can in fact decrease upon heating, such that increasing the temperature is generally not feasible. More serious solubility problems arise for block copolymers, where a common solvent for the different blocks must be found. Otherwise, the less soluble blocks aggregate, which leads to a highly viscous gel. Finally, cross-linked structures (elastomers) do not dissolve at all, but can only be swollen. In the latter cases, line-narrowing techniques adapted from solid-state NMR can, however, be used to obtain highly resolved solution-like spectra.

**Solution-State Studies**

The standard procedures of solution-state $^1$H and $^{13}$C NMR of small molecules may directly be applied to polymers, provided that a suitable solvent exists. Often, it is in fact not easy to prepare a polymer solution of sufficiently low viscosity, which is necessary to ensure rapid tumbling of the polymer coils as well as fast averaging over the different conformational states. Otherwise, broad lines or, for the case of fixed conformations, complex multiplet signals can challenge the interpretation of the spectra. In particular, solutions of high-molecular-weight polymers may be very viscous even under high dilution, requiring significant reductions of the concentration. Often, when the solvent is thermodynamically poor, the polymer tends to aggregate, again causing a broadening of the lines. Not uncommonly yet counterintuitively, the thermodynamic quality of a solvent can in fact decrease upon heating, such that increasing the temperature is generally not feasible. More serious solubility problems arise for block copolymers, where a common solvent for the different blocks must be found. Otherwise, the less soluble blocks aggregate, which leads to a highly viscous gel. Finally, cross-linked structures (elastomers) do not dissolve at all, but can only be swollen. In the latter cases, line-narrowing techniques adapted from solid-state NMR can, however, be used to obtain highly resolved solution-like spectra.

**Chemical Identification and Molecular Weight Determination**

Once a high-resolution spectrum can be recorded, the chemical identification is often straightforward. When the spectra are more complex than expected, the reason may be defects in a structure that was only assumed to be regular. For example, in vinyl polymers made from monomers of the type H–C═CHR, the common head-to-tail arrangement (…–CH$_2$–CHR–CH$_2$–CHR–…) may be disrupted by head-to-head units (…–CH$_2$–CHR–CHR–CH$_2$–…), which are easily distinguishable by the chemical shifts of the involved atoms, and their concentration is easily determined by integration. Similar arguments hold for the analysis of copolymer composition, where different modes of arrangement (different blockiness, e.g., …ABABAB… vs. …ABABABBBB…) lead to correspondingly different and potentially complex spectra. In general, such NMR studies of the chemical microstructure are commonly used to elucidate details of the mechanism of the polymerization reaction. Other areas of applications are the study of polymerization kinetics by...
real-time NMR, and of the chemical modification of polymers, for example, the substitution of side groups for property tuning.

An important aspect is represented by the chemically different and thus usually distinguishable end group signals. Provided that the polymer is linear or the degree of branching is known, integration of these signals and comparison with the main signals readily yields the degree of polymerization, and thus the molecular weight of the polymer (see Figure 6 for a similar application). However, as the end groups comprise only a small fraction of the overall signal, the method is limited to low to intermediate molecular weights, with the upper cutoff being determined by the dynamic range of the receiver and the resolution of the analog-to-digital converter of the spectrometer. Note that nowadays, hyphenated techniques, such as the combination of size-exclusion chromatography and NMR, have become commercially available. They even allow for detailed chemical analyses of the different subspecies in polymer mixtures or, in particular, of samples with broad distributions of molecular weight.

### Sequence Analysis

As explained in the first section, the proton or carbon chemical shifts of a polymer are sensitive to the stereochemical composition in much the same way as prochiral protons are distinguishable in small molecules. In polymers, such effects can be rather long-ranged (see Figure 2). Consider, for example, a vinyl polymer of the type \([\text{CH}_2=\text{CHR}–\text{CH}_2=\text{CHR}–\text{CH}_2=\text{CHR}–n]_n\). It is relatively obvious that the methylene (CH\(_2\)) signal will mainly distinguish the relative stereochemistry of the CHR units left and right of it; it is thus sensitive to a single (m or r) diad structure, with potential fine structure caused by tetrads (e.g., mmr). In contrast, signals from the CHR group are mainly split by the triad structure (mm, mr, or rr), as both the central stereocenter as well as the adjacent monomer units contribute. The fine structure then differentiates pentads, or even heptads in favorable cases. The fine structure due to pentad sequences is highlighted in Figure 4(b) on the example of the methyl resonances of atactic polypropylene. Note that these microstructural effects on chemical shifts ultimately arise from different Boltzmann weights for different conformational states, which in turn depend on the bulkiness and position of different substituents. The experimental shift thus arises as a fast-limit average, and sufficiently fast conformational dynamics, that is, the use of lowly viscous solvent or high temperatures is vital.

Once the signals are assigned to different sequences, the integrated signal can again be used to gain important knowledge on the polymerization mechanism. For example, if only the probabilities of formation of m or r diads upon attachment of a new monomer to the growing polymer chain are different, the probability to find specific triads, tetrads, and so on, which is directly proportional to the corresponding relative signal intensities, can be readily calculated from Bernoullian statistics. If the probability to form an m triad is given by \(p_m\), then \(p_r = 1-p_m\) and the triad probabilities are \(p_{mm} = p_m^2\), \(p_{mr} = 2p_mp_r\), and \(p_{rr} = (1-p_m)^2\). Therefore, in such a case, the intensities of the triad signals must be explainable by a single parameter, \(p_m\). If for chemical reasons, the attachment process is influenced by the stereostructure of a longer part of the chain end, a first- or higher-order Markov process determines the microstructure, and different independent conditional probabilities such as \(p_{m \rightarrow r}\) are necessary to explain the intensity distribution. Obviously, the longer-ranged the influence of the chain end structure on the attachment process is, the more independent probabilities are involved, and the higher is the required \(n\)-ad resolution to determine all these probabilities.

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**Figure 4** Twenty-five megahertz \(^{13}\text{C}\) NMR spectra of (a) isotactic, (b) atactic, and (c) syndiotactic polypropylene (PP: \(-\text{CH}_2–\text{CH}–\text{CH}_2\)\(_n\)). For the methyl groups in (b), the distinct regions of the different triad resonances are indicated, and the enlarged inset shows the resolution and assignment of pentad sequences. Reproduced from Tonelli AE and Schilling FC (1981) \(^{13}\text{C}\) NMR chemical shifts and the microstructure of polymers. *Accounts of Chemical Research* 14: 233–238, with permission from the American Chemical Society.
Relaxation Studies

It is well known from classical Redfield and Bloembergen-Purcell-Pound (BPP) relaxation theories that $T_1$ and $T_2$ relaxation times (as well as nuclear Overhauser enhancements) depend on the spectral density of molecular motion in the range of the Larmor frequency. In the case of polymers, solution-state relaxation studies therefore provide access to fast local segmental motions in the megahertz to gigahertz range, and to a limited degree also to the slower overall tumbling of the dissolved macromolecule as a whole. For the latter case, the relaxation data (relaxation times, preferably measured at different temperatures, Larmor frequencies, or both) can, for instance, be analyzed within the framework of the ‘model-free’ approach of Lipari and Szabo, originally established for proteins, which describes the dynamics in terms of two associated correlation times and an order parameter characterizing the spatial restrictions of the local segmental processes. More elaborate analyses require the consideration of additional motional modes, or even more accurately, a full spectrum of relaxation times, as predicted by established theoretical models of polymer dynamics.

Since fast local motions dominate the $T_1$ relaxation times and are usually characterized by large-amplitude conformational jumps, it is possible to use relatively

![Diagram](image)

**Figure 5** Investigation of dendrimer dynamics in solution by $T_1$ relaxation. (a) Schematic structure of a fourth-generation dendrimer and chemical structure of a PAMAM dendrimer, (b) $^{13}$C $T_1$ relaxation times (at 75 MHz) of terminal and internal sites as a function of PAMAM dendrimer generation, and (c) derived motional correlation times. Parts (b) and (c) reproduced from Meltzer AD, Tirrell DA, Jones AA, et al. (1992) $^{13}$C chain dynamics in poly(amide amine) dendrimers. A study of $^{13}$C relaxation parameters. *Macromolecules* 25: 4541-4548, with permission from the American Chemical Society.
simple one-component BPP expressions to obtain at least approximate correlation times of these motions, and compare them among different polymers for qualitative insights into their local dynamics in solution. A prominent example is shown in Figure 5 for the case of a specific class of macromolecules, namely dendrimers (or ‘starburst’ molecules), which are characterized by a regularly branched structure, with the number of branches growing regularly as a function of chemical generation. Note that the end groups, either unreacted or modified in the last step, are chemically distinguishable from the interior of the molecule.

A long-standing debate in polymer science was the question whether the end groups of such tree-like structures cluster together in a dense outer shell, leaving cavities in the inside of the molecule (as implied by Figure 5(a)), or whether the arms eventually fold back, leading to a homogeneous distribution of more freely mobile ends throughout the structure. The correlation times for local segmental motions in Figure 5(c), derived from the $T_1$ relaxation times in Figure 5(b), both plotted as a function of generation, immediately proved that the latter is in fact correct: The terminal sites move much faster, which would not be possible if they clustered in a dense shell.

**High-Resolution MAS Investigations**

Finally, as mentioned above, the solution-state studies highlighted in this section are not limited to actual isotropic, molecularly disperse solutions. In fact, the only important requirement is fast local mobility of the polymer, needed to achieve full conformational averaging. In many cases, the polymer in question may not be completely soluble, as is the case for block copolymers, aggregated systems in poor solvent, or most importantly, polymer networks. In all these cases, the polymer can only be swollen locally, that is, at least parts of the structure are surrounded by solvent and the segments move rapidly. On a larger scale, the tumbling of the respective substructure (aggregate, chain tagged to a surface of a network) is slow or even completely hindered. This leads to broadened spectra, where the line broadening arises from typical solid-state effects, that is, orientation-dependent interactions that are not averaged out completely, leaving on the solid-state scale a small, but potentially devastating residual broadening. Consequently, line-narrowing techniques from solid-state NMR, first and foremost magic-angle spinning (MAS), can be applied to very successfully remove this residual broadening and obtain spectra that are by and large comparable to solution-state spectra. This holds in...
particular for $^1$H spectra, which are hard to obtain at high resolution in a truly rigid solid. Note that MAS cannot remove line broadening arising from true relaxation effects such as slow conformational exchange. In such cases, temperature variation is the only remedy.

For the investigation of soft solid systems, MAS probes with very good magnetic field homogeneity (shim) and thus good spectral resolution, and a deuterium lock system for field stabilization, have recently become available for solution-state narrow-bore magnets under the label HRMAS, for high-resolution MAS. Spinning frequencies of a few kilohertz are usually sufficient to obtain spectra of solution quality, and HRMAS has gained popularity for the investigation of membrane- or carrier-bound but locally dissolved, thus mobilized, biological macromolecules.

Even without elaborate shimming and a lock, simple slow-MAS $^1$H spectroscopy, potentially using a cost-efficient narrow-bore MAS probe, allows for many fruitful applications in polymer science, and appears somewhat underestimated to date. An example is given in Figure 6, which shows solution-state and bulk-state MAS spectra of a vinyl-functionalized poly(dimethylsiloxane) precursor polymer, and the derived silicone elastomer after cross-linking with a bifunctional silane via a hydrosilylation reaction, respectively. Here, swelling of the elastomer to enhance chain motion is not even necessary, as the chains are very mobile (far above $T_g$) at room temperature. Figure 6(c) demonstrates that even the addition of solvent does not yield a spectrum with good resolution without MAS (dotted line), while the MAS spectrum is sufficiently resolved to identify all of the different functional groups. From this spectrum, the residual content of unreacted vinyl groups, as well as the content of –CH$_2$–CH$_2$– cross-linking groups, is straightforwardly obtained by integration. Therefore, the average cross-link density, inversely related to the molar mass of the different network chains, can directly be obtained from such spectra. There is, in fact, no other direct method that serves this purpose, since networks and elastomers are per se nonsoluble; alternatives are thermodynamic (swelling), mechanical, or NMR relaxation measurements, all of which are indirect and require calibration or models.

**Solid-State NMR**

The major challenges posed by bulk polymers are that they are either at least two-phase systems (semicrystalline or block copolymers) or they undergo dramatic changes in their properties with temperature at around the glass transition. Amorphous phases below $T_g$ and crystalline phases behave as rigid solids that require the full spectrum of methods from solid-state NMR, whereas soft melt-like phases (well above $T_g$) can in the NMR sense be treated as liquids, however with some residual solid-like properties. It is thus not uncommon that polymer scientists apply both solid- and solution-state experiments to their sample, to elucidate the potential multiphase character or to infer the ‘softness’ of the material on a molecular scale.

![Figure 6](image-url) **Figure 6** Low-resolution $^1$H NMR of semicrystalline polymers and networks. **(a)** FID of syndiotactic polypropylene at 382 K—the two-component decomposition (dashed line: melt signal extrapolation) indicates a crystallinity of ~20%. The inset shows the corresponding Fourier transform, with the shaded area as the (Gaussian) crystalline component. Data replotted from Maus S, Hertlein C, and Saalwächter K (2006) A robust proton NMR method to investigate hard/soft ratios, crystallinity, and component mobility in polymers. *Macromolecular Chemistry and Physics* 207: 1150–1158. **(b)** Linear correlation of the high-temperature plateau value of $T_2$ of thermoset epoxy networks with the number of bonds (~monomers) per network chain. The lines are fits to different models. Reproduced from Fry CG and Lind AC (1988) Determination of cross-link density in thermoset polymers by use of solid-state $^1$H NMR techniques. *Macromolecules* 21: 1282–1297, with permission from the American Chemical Society.
Low-Resolution $^1$H NMR

The simplest way to explore the multiphase character of a polymer system is to study its overall $^1$H relaxation behavior, often simply reflected in the time-domain free-induction decay (FID), or by lineshape analysis after Fourier transformation. Proton spectra, by virtue of the strong orientation-dependent homonuclear dipolar couplings among the many abundant spins, with coupling constants on the order of 30 kHz for two nearby CH$_2$ protons, are very sensitive to molecular motion. Large-amplitude reorientations exceeding $10^5$ kHz mark the transition into the soft, liquid-like domain, with substantially reduced couplings and thus narrower lines. In a semicrystalline polymer below $T_m$, with an amorphous phase well above $T_g$, a broad crystalline line (up to 50 kHz, due to multiple couplings) coexists with a narrower amorphous line ($\sim 10^2$ to $10^4$ Hz), which in the time domain corresponds to a rapidly decaying crystalline contribution ($\sim 20 \mu s$) and an amorphous part decaying in the milliseconds range. Simple decomposition into two components yields the approximate crystallinity in many cases. An example is displayed in Figure 7(a) for a measurement of syndiotactic polypropylene. Note that the detection of signal immediately after the excitation pulse is subject to a dead time problem (needed for pulse ring-down before detection can start), which must be overcome by suitable spin echo methods.

Such experiments are not restricted to semicrystalline polymers, but may also be of use for phase determination in phase-separated block copolymers or polymer blends, where the different components exhibit sufficient dynamic contrast. An important caveat is, however, the nontrivial, in most cases nonexponential, $T_2$ behavior in polymeric systems, leading to ambiguities in multicomponent fits. The transverse relaxation behavior of a rigid system is almost Gaussian, because the decay is not a true motion-induced $T_2$ process, but rather a dipolar dephasing (dipolar couplings cannot be refocused by a simple Hahn echo). A more mobile, amorphous phase can exhibit any decay shape between a Gaussian and an exponential, depending on whether the decay is dominated by residual dipolar couplings that arise from partially anisotropic chain motion or by the timescale of segmental fluctuations, respectively. Sample heterogeneity, such as mobility gradients, also plays a role here. This means that the apparent $T_2$ mostly has only heuristic value – the decay curves are hard to interpret quantitatively.

The relaxation behavior of networks or elastomers is usually completely dominated by residual dipolar couplings, as network chains are fixed at both ends and can never move isotropically. This is why $T_2$ in networks approaches a high-temperature plateau when heated sufficiently far above $T_g$ where the segmental motion is too fast to exert an appreciable influence. In this regime, the apparent $T_2$ is inversely proportional to the average residual dipolar coupling constant, which in turn is inversely related with the number of monomers in a network chain. An example is shown in Figure 7(b). Therefore, $T_2$ results are directly related to the mechanical properties of elastomers, in that they provide molecular-level information on the cross-link density. Yet, as stated above, a direct conversion requires many model assumptions. Nowadays, much more elaborate multiple-quantum experiments provide a more direct and quantitative means to not only measure residual dipolar couplings, but also assess aspects of its distribution. In this way, details on the microstructure of networks have become accessible.

The fact that a mesoscale motional anisotropy, leading to residual couplings, plays a role in such experiments means that they provide information on the chain dynamics on a semilocal scale. $T_2$ and related phenomena are thus not only useful for the study of elastomers, but also provide valuable tools to study, for instance, the dynamics of the amorphous/mobile chains in semicrystalline polymers or block copolymers, and of entangled polymer melts. Complementarily, the timescale and details of fast segmental motions are well in the ‘liquid’ range, and may be studied by $T_1$ relaxation, and in combination, polymer dynamics can be studied over several orders of magnitude in time. It should be noted that such experiments do not necessarily require superconducting high-field spectrometers – cost-efficient, low-field equipment is often fully sufficient, as the effects in question are based on dipolar couplings and are thus field independent. This of course only holds if chemical resolution is not necessary.

The low-resolution assessment of phase composition in any heterogeneous polymer system is of course critically based on sufficient mobility contrast. If, for instance, the amorphous phase of a semicrystalline polymer is not mobile enough, and temperature variation would alter the structure or the morphology, high-resolution $^{13}$C spectroscopy is inevitable.

High-Resolution $^{13}$C NMR

High-resolution $^{13}$C NMR spectroscopy in solids is commonly achieved by MAS in combination with high-power dipolar decoupling (DD) and cross polarization (CP). MAS and DD provide spectral resolution, that is, they split up the wide and, in polymers, often featureless powder line shapes into relatively narrow lines. Although MAS-DD spectra often do not reach the line resolution of solution-state spectra (the line width in solids is on the order of few parts per million, whereas in liquids it is...
typically down to 0.1 ppm), they still provide useful spectral information. First, the larger line width is often due to distributions in conformations, thus it carries information on disorder. In fact, the $^{13}$C lines of crystalline phases in semicrystalline polymers are often almost as narrow as solution-state lines. Second, the line width must be considered in relation to the overall chemical shift range of approximately 200 ppm and compared with the very limited resolution of $^1$H solid-state spectra, which — even under very fast MAS or multipulse line narrowing — exhibit line widths on the order of 1 ppm on a chemical shift scale of only approximately 10 ppm.

CP, on the other hand, permits a substantial shortening of the experimental time, as it produces a stronger signal (theoretically up to a factor of 4 for $^{13}$C, practically between 2 and 3, as compared to direct $^{13}$C excitation) and permits a shorter repetition time between subsequence signal averages due to its dependence on the shorter $^1$H $T_1$, which is approximately one order of magnitude shorter than the $^{13}$C $T_1$, which in turn governs the repetition time of directly excited $^{13}$C spectra. MAS and DD had already been combined with CP in the 1980s, and still represent the major methodology for almost all solid-state $^{13}$C experiments. A comparison of CP spectra with DD (removing dipolar couplings), with and without MAS (removing the $^{13}$C chemical shift anisotropy), is presented in Figure 8. The dramatic increase in resolution (accompanied by a large time saving) is readily apparent.

Although, owing to the limited resolution, information on the monomer sequence is hard to obtain from solid-state spectra, supramolecular structural features such as amorphous or crystalline phases are more easily recognizable. Usually, chemical segments in the crystalline phase are more rigid or they feel a chemically similar environment, leading to relatively narrow lines, whereas segments in the amorphous phase are in a disordered environment, leading to a distribution of isotropic chemical shifts and broad lines, which might additionally be subject to dynamic broadening. Thus, depending on temperature, the molecules exhibit a molecular mobility in the kilohertz range, which interferes with the line narrowing by MAS and DD and leads to temperature-dependent line broadening. As an example, Figure 9 shows the structure of the crystalline phase of a specific semicrystalline polyolefin, the crystallite chains of which form $\gamma$ helices. The broad bases of the lines in the $^{13}$C CPMAS spectrum (dotted ellipses) arise from contributions of the amorphous phase, which can be suppressed by a relaxation filter.

The authors would like to draw the attention to a comparison between the inset of Figure 7, where the amorphous and crystalline components were assigned to the narrow and wide proton subspectra, respectively, and the just explained reversed assignment in the carbon spectrum. The apparent contradiction can be understood on the basis of the dynamic properties of the different phases and the different origins of line broadening in $^1$H and $^{13}$C spectra: the molecules in the crystalline phase are rigid and experience a large $^1$H-$^1$H dipolar coupling, resulting in a wide $^1$H spectrum that is almost entirely governed by this interaction, whereas the higher mobility of the molecules in the amorphous part partially average this coupling, resulting in a narrower line. This assignment is generally valid, and challenged only in cases where $T_g$ of the amorphous phase is not low enough to render it sufficiently mobile.

In $^{13}$C spectra, however, the dominant interaction is the isotropic chemical shift of the carbons, since the anisotropic chemical shift as well as the dipolar couplings are (usually) efficiently suppressed by MAS and DD. Thus, the line widths are determined by the degree of order of the local environment of the probe nucleus, explaining the reversed assignment.

This component assignment in $^{13}$C spectra is, unfortunately, not unique. In unfavorable cases, amorphous
and crystalline line widths and positions can in fact be hardly distinguishable. A particularly unusual case is poly(ethylene oxide), where the assignment of the room temperature $^{13}$C spectrum is again reversed, as the crystalline resonance is extremely broad due to intermediate (kilohertz) mobility of the chains in the crystallites (helical jumps) that interfere with the decoupling and MAS (details on such motional broadening effects are addressed in the next section). In addition, the crystalline helix in this polymer is disordered, such that the line remains $\text{B}^{3}$ ppm broad even at low temperature when the chain motion is slowed down. From this example, it could be noted that complex motional effects and other origins of line broadening may always contribute to the line widths of carbon MAS spectra of polymers, and must be carefully considered and explored, for example, by temperature variation.

P0155 Given the lack of or an ambiguity in spectral distinction between different phases or components, their separation can be aided by relaxation-time filters that are based on different mobilities. The easiest of these is a simple change in the repetition delay between subsequent scans for signal averaging (corresponding to a $^1\text{H} T_1$ filter when CP is used, or a $^{13}\text{C} T_1$ filter in case of direct excitation). A good general way to explore coexisting mobile amorphous and rigid crystalline or glassy regions (in semicrystalline polymers or block copolymers, respectively) is to simply compare $^{13}\text{C}$ direct excitation spectra with repetition delays on the $1\text{s}$ timescale (emphasizing mobile amorphous regions), and CPMAS spectra with short CP (emphasizing rigid regions). Other possibilities are, for instance, using the different $T_{1\rho}$ of either $^1\text{H}$ or $^{13}\text{C}$ by changing the CP spin-lock time, or exploiting $T_2$ differences by adding Hahn echo delays on either channel (either before or after the CP). An example of a $T_{1\rho}$ filter procedure for component separation in a semicrystalline polyolefin is presented in Figure 9(c).

Multidimensional $^{13}\text{C}$ NMR

It is obvious from the above that in solid-state $^{13}\text{C}$ spectra, the structural information (provided by the isotropic chemical shift value) is often concealed by dynamic information, which arises from different degrees of averaging of anisotropic interactions by molecular motions. Such interactions are the anisotropic chemical shift and the homo- and heteronuclear dipolar coupling, as well as the quadrupolar coupling when nuclei with $I > 1/2$ are measured (this will be addressed in the next section). Basically, all these interactions (except the quadrupolar coupling) contribute to the appearance of the $^{13}\text{C}$ spectrum and in principle, the spectra can be simulated to determine the different contributions and to extract the desired information. Note that even indirect couplings, such as $^1\text{H}-^1\text{H}$ homonuclear dipolar couplings, affect $^{13}\text{C}$ spectra in a way that they interfere with the efficiency of DD and increase the line width.

However, in particular under conditions of finite signal-to-noise and due to the large number of potentially involved spins and the complex dynamics, full spectral simulation is in practice almost impossible. Instead, it is desirable to separate the different effects in different (spectral or time) dimensions of multidimensional experiments. The probably simplest example is the acquisition of $^{13}\text{C}$ CP spectra as a function of the above-mentioned relaxation filter durations, incremented in regular intervals. One can then achieve a component
decomposition of the spectrum and at the same time estimate the respective relaxation times.

Turning to ‘true’ 2D spectroscopy, such experiments can, for instance, correlate the isotropic chemical shift in one dimension with the anisotropic chemical shift or heteronuclear dipolar coupling in a second dimension. The latter are termed ‘separated local field’ (SLF) experiments, and are among the most popular approaches, because they are robust, easy to implement and require standard hardware only. Last but not least, the heteronuclear dipolar interaction is well defined (as it reflects the arrangement of heterospins in the immediate surroundings of the nucleus) and thus easy to interpret. A particularly simple and correspondingly popular sequence is the so-called WISE (wideline separation) experiment, which is not strictly an SLF experiment, but similar to it, in that it correlates the carbon CPMAS spectrum with the $^1$H wideline spectrum of the protons closest to the carbon. The pulse sequence is identical to the CPMAS sequence with a short CP time (for local transfer), with the only difference that an incremented delay is inserted between the first $^1$H pulse and the CP spin lock, during which the $^1$H FID is probed. The pulse sequence, as well as typical proton and carbon spectra along with their separation in a 2D WISE spectrum, is depicted in Figure 10.

As mentioned already in the preceding section, a very simple alternative and the most recommendable first approach to assess dynamic heterogeneity is to compare CP spectra acquired with rather short contact time (polarizing only rigid, strongly dipolar-coupled $^{13}$C) with one-pulse direct-polarization spectra taken with a short recycle decay on the order of a few seconds (emphasizing signals from highly mobile liquid-like $^{13}$C with correspondingly short $T_1$). With such experiments, or by comparing the wide or narrow lines in the proton dimension of 2D WISE spectra, it is very easy to distinguish carbons from rigid and mobile domains. However, even from the resolved proton line shapes, it is difficult to draw truly quantitative conclusions, since the homonuclear $^1$H-$^1$H coupling involves many nuclei and is hard to simulate correctly.

More elaborate, true SLF experiments utilize $^1$H homonuclear decoupling, which leaves the $^{13}$C-$^1$H dipolar interaction as the only remaining coupling for the second dimension and thus, provide a much clearer picture. Examples are the DIPSHIFT (correlation of dipolar and chemical shift information) and LG-CP (Lee-Goldburg cross polarization) experiments. The latter is in fact just a more quantitative version of the traditional CP experiment, in which the $^{13}$C-$^1$H dipolar coupling is extracted from the intensity buildup as a function of the variable CP time. Such experiments are also particularly suited for the quantitative measurement of residual heteronuclear dipolar couplings, as addressed below.

Figure 10  (a) Pulse sequence of the WISE experiment. Typical magnetization decays are shown for mobile (full line) and rigid components (dotted line). (b) $^1$H (left) and $^{13}$C spectrum (right) of a 1:1 blend of poly(styrene) and poly(vinyl methyl ether). The $^1$H spectrum is the superposition of wide and narrow components that originate from the different polymers, due to their different mobilities. They cannot be distinguished here, whereas in the $^{13}$C spectrum the resonances of the two polymers are well separated. These two different sets of information can be nicely separated in the 2D WISE spectrum (c). Reproduced from Schmidt-Rohr K, Clauss J, and Spiess HW (1992) Correlation of structure, mobility, and morphological information in heterogeneous polymer materials by two-dimensional wideline-separation NMR spectroscopy. Macromolecules 25: 3273–3277, with permission from John Wiley & Sons Ltd.
Dynamic and Exchange NMR

As already alluded to, indirect structural information can also be inferred from dynamic data, for example, from the different mobility of molecules residing in amorphous or crystalline phases. Thus, and in particular due to the fact that many mechanical properties depend crucially on the molecular mobility of the polymer chains, it is desirable to determine the kinetic parameters quantitatively, that is, both amplitudes and time constants. Molecular dynamics in polymers spans a wide range of correlation times, from very fast processes on the order of pico- and nanoseconds, up to slow motions on the order of milliseconds or even seconds. To cover this entire range, different techniques have to be applied.

For fast processes, relaxation techniques as explained in the Solution-State Studies section can be employed. Additionally, the measurement of partially averaged anisotropic couplings is particularly informative in this regime, as in solids or soft semisolids (such as glassy or rubbery polymers), and in contrast to the liquid state, anisotropic motions do not average the interactions completely, even though they may be very fast. The degree of averaging depends on the amplitude of the motional process and is commonly parameterized by a so-called dynamic order parameter, which is just the ratio of the measured, partially averaged coupling to the value for a completely rigid segment, that is, the full coupling. For specific models, the order parameter can be recast into amplitudes of motion, however, in most cases, the order parameter itself, and its temperature dependence or the comparison between different samples, provides useful information.

So-called intermediate motions with correlation times in the microsecond range can be easily recognized from the temperature dependence of the carbon spectra, as the molecular process occurs on the timescale of the lifetime of the NMR signal (as reflected in the $T_2$ relaxation time, or the decay time of the FID). In combination with high-resolution line-narrowing techniques such as MAS or DD, it has to be kept in mind that these remove contributions from the anisotropic chemical shifts or dipolar couplings by modulating the spin interactions (either in real space or in spin space, respectively) with a typical frequency (the MAS rotation frequency or the nutation frequency of the $^1$H irradiation, respectively). Now, if the inverse of the correlation time of the molecular motion approaches these modulation frequencies, the efficiency of the line-narrowing mechanism deteriorates and a so-called dynamic line broadening appears, permitting a simple qualitative assignment of a correlation time to the inverse modulation frequency at the temperature at which the maximum broadening appears.

More quantitative information can be obtained from the comparison of calculated/simulated spectra with experimental ones, and the application of SLF experiments in this dynamic range. However, the by far most accurate approach for intermediate motions is the acquisition of $^2$H spectra and the comparison with calculated line shapes. These experiments have an inherently low resolution, as the lines are very broad (but well structured), and the price to pay is the effort in the preparation of selectively $^2$H labeled substances, in order to study the motional processes with molecular resolution. On the positive side, the $^2$H quadrupolar interaction as the dominant spin interaction is an extremely local and well-defined dynamic probe, as it is merely sensitive to orientations of the (asymmetric) local electronic environment of the nucleus, and the spectra can therefore be simulated rather accurately. This is demonstrated in Figure 11 for local motions in glassy poly(carbonate), where the different chemical groups

![Figure 11](image-url)
have been labeled and studied separately. The thus-
quantified phenyl flip motion is in fact an important
contributor to the efficient dissipation of mechanical
energy in this high impact strength polymer.

On the slow end of the dynamic range of NMR ex-
periments are the so-called exchange experiments, which
are capable of detecting molecular reorientations that
occur on timescales much longer than $T_2$. Such motions
do not lead to notable spectral changes. Exchange NMR
relies on the fact that molecular orientations are encoded
in NMR frequencies via anisotropic interactions, and that
any change in molecular orientation results in a change
in the resonance frequency of the probe nucleus, in
principle on any timescale. A technique that can detect
d these frequency changes can thus be used to detect such
dynamic processes. The general principle is always that
after measuring the interaction frequency ($\sim$ orientation)
during an evolution delay, the magnetization is stored
along the magnetic field axis (along $z$) by a 90° pulse. It is
then read out again after a mixing time that is limited
only by the (often very long) $T_1$ relaxation time, and a
second frequency measurement (most often just a spec-
trum acquisition) follows right after.

These experiments are therefore most often two-di-
imensional: NMR data (FIDs) are sampled in two time
dimensions that are separated by a freely chosen mixing
time, during which the molecular dynamic process can
occur. A two-dimensional Fourier transform correlates
the data from the two time domains in a 2D spectrum,
and whenever a process has changed the molecular
orientation, peaks off the main diagonal of the spectrum
immediately reveal the dynamic process. The widespread
application of such methods started out in the 1980s, with
applications of $^2$H- and $^{13}$C-CSA-based methods,
prominently by the Spiess group, and MAS variants for
$^{13}$C samples in natural abundance. An example for the
former is shown in Figure 12, where the more compli-
cated phenyl ring motion in poly(styrene) is elucidated
by 2D $^2$H exchange methods on the slow (low-tem-
perature) end, and is complemented by information from
other dynamic NMR experiments in order to charac-
terize the process over almost 10 orders of magnitude in
time. It should be noted that the off-diagonal intensity
distribution in the 2D spectra sensitively encodes the
reorientation angle, which is in this case distributed over
a wide range, as the underlying process corresponds to
rotational diffusion.

On the down side, the 2D acquisition scheme renders
the 2D approach rather time consuming, and as one of
the most recent improvements, the so-called CODEX
sequence, illustrated in Figure 13, was established as an
easy-to-implement and robust one-dimensional MAS
method that permits the reliable determination of both
the correlation time of motion as well as its amplitude in
natural isotopic abundance. In this high-resolution 1D
method, the sampling of the time-domain signal in the

![Figure 12](image-url)
indirect dimension is replaced by a fixed evolution time during which the magnetization can acquire a certain phase, arising from the anisotropic chemical shift (CSA) frequency, thus encoding the molecular orientation. The same is done after the mixing time, and the signal intensity in the highly resolved $^{13}$C spectrum finally depends on whether the nucleus in question along with its anisotropic shielding environment has rotated or not. The $180^{\circ}$ pulses during these periods manipulate the acquired phase, in a sense that they actually reverse the averaging by MAS (which would in principle preclude the CSA measurement, see Figure 8). This is called 'recoupling' and represents a very general technique often applied in solid-state MAS NMR. The length of the evolution/recoupling time necessary to observe the exchange process is in fact a quantitative measure of the motional amplitude, and actually provides an even better sensitivity for small-amplitude motions as compared to traditional static 2D exchange spectroscopy.

**Spin Diffusion NMR**

Truly structural methods are the so-called spin diffusion experiments, which can be used to determine domain sizes in materials that are not suited for scattering studies (e.g., by missing long-range order). Spin diffusion is an effect driven by homonuclear dipolar interactions between abundant spins, mostly protons, by which magnetization is transported between spatially fixed spins over distances as large as some 100 nm by a quantum-mechanical flip-flop process. It can in fact be measured with the same one- or two-dimensional versions of exchange spectroscopy mentioned above, just because spin diffusion occurs on similar, rather long timescales between the $z$ components of differently polarized spins. Spin diffusion is often a competing process to dynamic exchange, and temperature variation can be used to distinguish between the two: spin diffusion is only weakly temperature dependent, and if at all, the process becomes slower with increasing temperature, due to dynamic averaging of the dipolar interaction that is responsible for it.

A typical experimental scheme is shown in Figure 14. Two phases A and B that can be discriminated by their NMR parameters (e.g., crystalline and amorphous), in this case by the resonance frequencies, contribute to the NMR spectrum. By a selection process that can be realized either by selective excitation or the application of relaxation filters or dipolar filters, a single component (in this case A) is selected. Then the magnetization is permitted to spread by spin diffusion throughout the sample during a mixing time, and eventually, the

![Figure 13](image)

**Figure 13** Pulse sequence and data of the 1D MAS exchange experiment CODEX, as applied to slow motions in the crystalline phase of a polyolefin. (a) Pulse sequence ($^{13}$C channel only). The essential parts are the mixing period $t_m$, which is sandwiched between two recoupling cycles, applying trains of rotor-synchronized $\pi$-pulses. (b) To extract the correlation time of motion, the number of recoupling cycles is kept constant while the length of the mixing period $t_m$ is incremented logarithmically. The longer the $t_m$, the more molecules perform a reorientation, leading to signal decay. The straight line is a fit to a stretched exponential function yielding the average $\tau_c$. (c) For information on amplitude of motion, $t_m$ is kept constant at a value larger than $\tau_c$ and the number of recoupling cycles is incremented. For more details, see Miyoshi T, Pascui O, and Reichert D (2002) Helical jump motion in isotactic-poly(4-methyl-1-pentene) crystallites revealed by 1D-MAS exchange NMR spectroscopy. *Macromolecules* 35: 7178–7181.
polarized B spin signal reappears in the spectrum. Given a dynamically heterogeneous multiphase structure, such experiments can in fact be performed under low-resolution conditions (see Figure 7), using the mobility contrast both for the phase-specific selection of magnetization, as well as for the component-specific detection.

The experiment is repeated for different mixing times, and the increase of the B component or the decay of the A component yields information on the domain sizes, provided the NMR parameters (i.e., the spin diffusion coefficients) and the overall structure of the phases (1D diffusion in a lamellar system vs. 2D diffusion among cylinders, etc.) are known. Another distinguishing factor is that spin diffusion is described by a square root of time law in its initial stages (cf. the Einstein-Smoluchowski equation), whereas a dynamic exchange process follows an exponential rate law, which is linear in the early stage. Thus, a linear behavior in a plot of the intensity versus the square root of time reveals a spin diffusion process, and the initial slope encodes the size of the domain, as is apparent from Figure 14(b).

**Figure 14** (a) Schematic representation of \(^1\)H spin diffusion in a two-phase system with spatially constant proton density. After the selection period, protons are polarized only in one phase A, and the NMR spectrum only shows the corresponding signals. The redistribution of magnetization by \(^1\)H spin diffusion is monitored in the spectrum: with increasing mixing time, the intensity of signals corresponding to the selected region A decreases, whereas the signal intensity of the initially depleted region B increases. (b) Spin diffusion diagrams as obtained for different PS-PMMA block copolymer samples. The values at the simulation curves indicate the long periods \(d_a + d_b\). Reproduced from Clauss J, Schmidt-Rohr K, and Spiess HW (1993) Determination of domain sizes in heterogeneous polymers by solid-state NMR. Acta Polym. 44: 1–17, with permission from Wiley Interscience.
Oriented Polymers

Last but not least, it is possible to make use of the orientation dependence of the NMR resonance frequency to obtain information on molecular orientations in anisotropic polymeric systems such as stretched polymers or fibers. Since the resonance frequency of a nucleus is – for anisotropic interactions – determined by its orientation versus the external magnetic field, it is obvious that the distribution of orientations immediately shows up in the solid-state NMR spectrum. Such studies are limited to samples where dynamic effects on the spectra are absent, that is, the samples are either completely rigid (e.g., cooled below $T_g$), or motions that are present must be anisotropic and in the fast limit (e.g., methyl rotation or phenyl flips).

The principle of the approach is illustrated by perfect powder spectra (‘Pake’ patterns) such as the CSA pattern of the carbonyl carbon in Figure 8(a) or the quasi-static (pre-averaged) $^2$H spectrum of the methyl group in Figure 11, which only arise if the distribution of different orientations in the sample is completely isotropic. Any such prototypical solid-state spectra become distorted once a macroscopically oriented or otherwise ordered sample is measured: if not all orientations are present with the same probability, the deviations of the spectral shape from the Pake pattern arise and allow for a quantitative extraction of the orientation distribution. Even better quantification is possible if spectra with different orientations of the magnetic field with respect to the sample axes (e.g., the stretching direction) are acquired and analyzed simultaneously. A limiting case is represented by liquid-crystalline systems, which often orient perfectly in the magnetic field, or simply by single-crystal samples, where the Pake spectrum is reduced to a single line (or a single splitting), corresponding to a single orientation. Observing and analyzing spectra at different sample orientations is often referred to as ‘NMR crystallography’.

As is also obvious from the two figures addressed, again, $^2$H is the most useful nucleus for such investigations, since the quadrupolar interaction is strictly local, large, and dominant (whereas the CSA spectrum can be broadened by imperfect decoupling, conformational disorder, etc.). Further, the orientation of the quadrupolar symmetry frame is in good approximation parallel to the chemical bond that connects the deuteron to the rest of the molecule, rendering a quantitative interpretation of the orientation distribution rather straightforward. Again, the price to pay is the synthetic effort to label the polymers with $^2$H. However, multidimensional (recoupling) MAS methods, which work for $^{13}$C in natural abundance, have also been applied for this purpose. In this case, numerical procedures to extract structural information from the intensities of specific spinning sidebands are needed, and are often less quantitative than fits to perfect static $^2$H spectra.

Further Reading