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The NMR of solid polymers: an overview

1.1 The nature of polymers

One of the remarkable features of current progress in materials technology is the ever-increasing ability to control and design the physical and chemical responses of synthetic polymers. An unprecedented range of properties is now routinely accessible through a variety of processing techniques which include chemical synthesis and substitution, thermal and electrical treatment, addition of fillers, blending of dissimilar polymers and mechanical deformation to name but a few.

Polymers are long chain molecules comprising large numbers of basic repeat units: the chemical structures of some of the more common types are furnished in table A1.1 (Appendix 1). For the most part, they are organic materials of high molecular weight in crystalline, glassy or rubbery states, one or more of which may be simultaneously present. Attempts to understand more fully the underlying reasons behind the properties of polymers are bedevilled by a characteristically complex morphology which defies precise description even in the chemically simplest cases. There is concomitant complexity too in the way in which polymer molecules move. Motions of flexible backbone chains, for example, derive from many coupled degrees of freedom and there is often a broad distribution of spectral frequencies associated with a given motional event. Two or more discrete motions may be active at the same time.

It is important to understand structure and motion in polymers because of the manner in which they influence properties of practical interest. Changes in crystallinity or tacticity, for example, can induce marked differences in overall performance and potential applications of a polymer; chain orientation can confer remarkable strength as in ultradrawn polymers; plasticisers and fillers alter mechanical properties; molecular

motion underpins thermal distortions, creep and impact strength; the motion of molecules with dipole moments influences electrical loss; and control of morphology and material defects is the key to improving the performance of semiconducting polymers and so on.

In discussing the application of NMR to the study of polymer systems, the somewhat crude though pragmatic approach of distinguishing between *structure* and *motion* is adopted even though the two are inevitably mutually interdependent. Indeed it is often the case that different structural regions in a polymer are identified precisely on the basis of their characteristically different motions. It is a matter of convenience, in the interests of clarity of presentation, to retain this arbitrary dichotomy between structure and motion, at least for the time being, subject to the proviso that the strong inter-relationship between the two is constantly borne in mind.

1.2 The role of NMR

NMR spectroscopy has featured prominently among the host of investigative techniques used in polymer research. One consequence of the short-range nature of NMR interactions is the inherent sensitivity to different molecular environments as typically reflected in NMR lineshapes and decays (fig. 1.1(a)); but, as with most forms of experimental data, the translation of raw NMR results into meaningful information on structure and molecular relaxation is not wholly unambiguous. In particular, interpretation of low-resolution NMR spectra where lineshapes are dominated by dipolar contributions inevitably appeals to intuitive models which lead to conclusions that are not always definitive. While the onset of motion can be readily detected, the precise mechanism is often obscure. This contrasts with the identification of individual chemical sites in high-resolution spectra for liquids in which the usually dominant dipolar interactions are averaged to zero as a gift of nature. Consider, for example, the high-resolution proton spectrum of a moderately low molecular weight ($M_n = 2600$) polybutadiene terminated at both ends with phenyl groups (fig. 1.1(b)). CH_2 , CH and phenyl protons, for which experimental intensities agree rather well with theoretical estimates, are readily discernible. That the relaxation behaviour of the resolved moieties can be individually explored greatly facilitates the study of chain dynamics.

Selective suppression of the dominant dipolar contribution to the Hamiltonian in the solid state reveals a wealth of information associated with the weaker chemical shift and J -coupling contributions. This has been achieved by means of cross polarisation (CP), dipolar decoupling (DD)

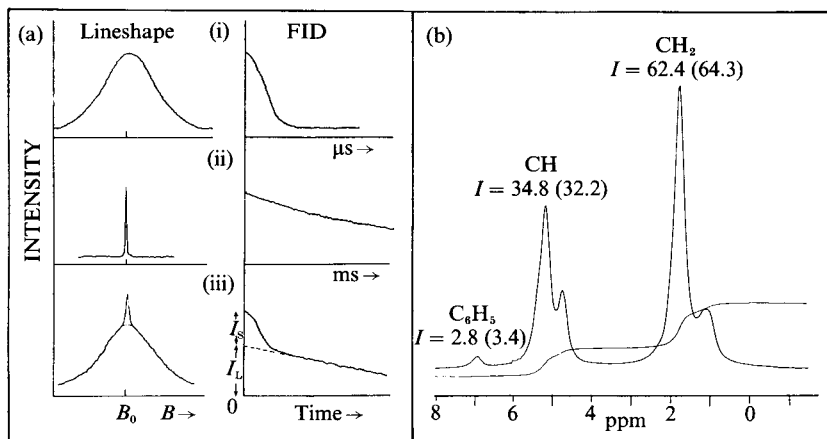


Figure 1.1. (a) Schematic lineshapes and corresponding free induction decays (FIDs) for (i) a solid, (ii) a liquid and (iii) a material such as a partially crystalline polymer that contains both rigid and mobile molecules. The timescales for the solid and liquid FIDs are of the order of microseconds and milliseconds, respectively. The initial component intensities of the composite FID and, correspondingly, the areas under the resolved lineshapes, denote the number of participating resonant nuclei contributing to each phase. (b) Proton spectrum (300 MHz) of a moderately low molecular weight ($M_n = 2600$) polybutadiene terminated at each end with a phenyl group (25% *trans* 1,4, 50% vinyl, 99% unsaturated). Experimental intensities, I , are computed automatically by the spectrometer from the areas under the component peaks. The theoretical components (in parenthesis) are computed as follows: $10/(6n + 10)$ phenyl protons; $2n/(6n + 10)$ CH protons; $4n/(6n + 10)$ CH_2 protons where $n = 45.3$ is the number of butadiene units in the chain. Proton chemical shifts are relative to TMS.

and magic-angle spinning (MAS) techniques. Table 1.1 illustrates the progression towards ^{13}C spectra in solids (cf fig. 5.1). However, because MAS averages out anisotropic spin interactions there is a loss of important information on the structural and motional complexity in the solid state, information which is vital to the complete characterisation of solid polymers. Separated local field and rotational spin echo experiments (Opella and Waugh, 1977; Munowitz and Griffin, 1982; Schaefer *et al.*, 1983) were among the early successes in retrieving this suppressed information. More recent developments in multidimensional NMR allow different spin interactions to be correlated or separated, exchange between different states of a resonant nucleus to be monitored over selected time periods, and the details of complex motions to be elucidated (Ernst *et al.*, 1987; Nakai *et al.*, 1988b; Spiess, 1991). The term *nuclear magnetic resonance crystallography* has been coined to describe one form of two-dimensional NMR which can elucidate the relative orientations and

Table 1.1. *Solution state versus high-resolution solid-state ^{13}C NMR spectroscopy*

Total interaction	=	Zeeman (MHz)	+	Dipolar ^(a) (kHz)	+	Scalar ^(a) (Hz)	+	Chemical shift
Solution state		50		0		200		isotropic, single frequency
Solid state		50		50		200		200 ppm-wide chemical shift anisotropy
Solid-state NMR				high-power (dipolar) proton decoupling		high-power decoupling also removes <i>J</i> coupling		magic-angle spinning gives the isotropic line

^(a) Couplings are to ^1H .

internuclear distances of neighbouring molecules in polycrystalline and non-crystalline solids (Tycko and Dabbagh, 1991; Raleigh *et al.*, 1989). Selective isotope labelling and the ability to control spin diffusion (which tends to average out much detailed information) have also resulted in more meaningful data for comparison with theoretical models.

Efforts to unravel the complexities of polymer behaviour are also eased by correlating the relaxation results of NMR with those of related techniques which include dielectric relaxation, dynamic mechanical thermal analysis (DMTA) and quasi-static experiments such as differential scanning calorimetry (DSC). Each technique responds in its own characteristic manner. For example, NMR and DMTA are sensitive to the motion of CH₃ and CH₂ groups, whereas dielectric relaxation is not since groups such as these do not have a dielectric moment. DMTA probes a wide range of low frequencies typical of those which influence impact strength and which are not systematically accessible by other methods. In general, it transpires that many diverse macroscopic properties of a polymer reflect the same relaxation mechanism which, in turn, can be identified with a specific molecular motion (cf Section 1.5).

1.3 Structural considerations: a model for the polymer

Despite the inherent structural complexities of polymers, the use of idealised models that are generally consistent with the known morphology has facilitated the interpretation of experimental data. A two-phase model was first proposed to account for the readily discernible behaviour of crystalline and amorphous regions in a partially crystalline polymer (Wilson and Pake, 1953). Spectra consisted of superimposed broad and narrow resonances, assigned respectively to crystalline and amorphous regions (fig. 1.1(a)). The implicit assumption of sharp boundaries between the two phases has since been refined in those cases where interfacial material is present in such proportions as to constitute a third phase (fig. 1.2). This general approach carries over naturally to a treatment of composites such as block copolymers and heterogeneous blends.

However, the interpretation of experimental data in terms of non-interacting phases is compromised by evidence of transport between crystalline and amorphous phases (Mansfield, 1987; Schmidt-Rohr and Spiess, 1991b) and by a number of factors that are inherent features of NMR. Spin diffusion, for example, can affect the magnitudes and intensities of component spin–lattice and rotating frame relaxation times in

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Vincent J. McBrierty and Kenneth J. Packer

Excerpt

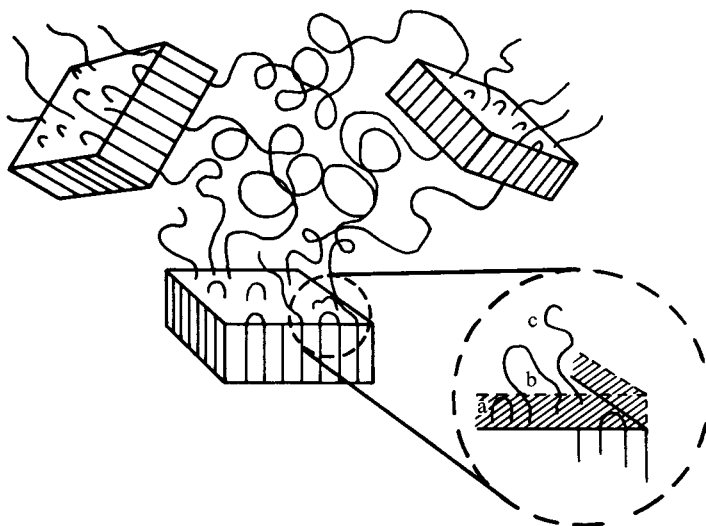
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Figure 1.2. Visualisation of crystalline and amorphous material in a partially crystalline polymer. (a) tight fold; (b) loose fold; (c) cilium or part of a tie molecule. It is possible, on occasion, to resolve an interfacial phase on the surface of the crystalline component as defined by the dashed region in the insert.

a way that complicates the quantitative analysis of separate phases (cf Section 3.8.3). The observation of complex relaxation decay may be an inherent feature of NMR relaxation behaviour itself rather than a manifestation of distinct morphological regions or structural entities in the polymer. The observed decay may also arise from a broad distribution of structural environments (or a broad distribution of motional correlation frequencies) and the extraction of only two or three components may simply reflect the limitations of the decomposition procedure rather than a definitive indication of the presence of a specific number of discrete regions or molecular entities as such.

Although there are obvious limitations in the approach, the description of a polymer in terms of one or more non-interacting phases forms the basis of a rational and consistent interpretation of experimental NMR data. To a first approximation, it is presumed that each phase is made up of characteristic structural units in the form of isotropic amorphous material, single crystals, crystallites, chain segments or other appropriate structural entity. The properties of units with well-defined crystallographic structure tend to be spatially anisotropic and in this respect the NMR response is no exception. Lineshapes for single crystals, for example, often

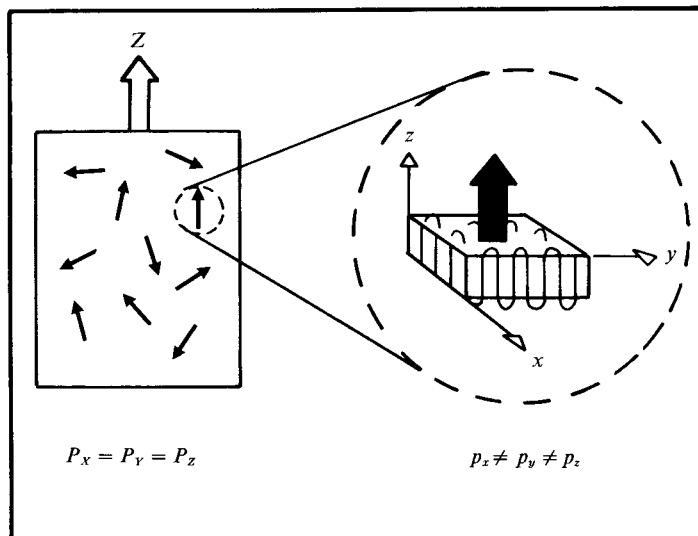


Figure 1.3. Schematic diagram showing the spatially random orientation of structural crystal units in an isotropic bulk polymer. The arrows denote the polar axes of the units. At the macroscopic level, the property, P , under examination does not depend on direction because of spatial randomisation in the bulk. At a molecular level, the tensor property is generally anisotropic, that is, $p_x \neq p_y \neq p_z$.

depend sensitively upon sample orientation in the laboratory magnetic field. In bulk materials, on the other hand, the constituent structural units are randomly distributed in space and, as such, the macroscopic measurement represents an isotropic spatial average for the system as a whole (fig. 1.3). Consequently, much useful information contained in the molecular anisotropy is lost in macroscopic measurements on isotropic polymers. The situation is redressed somewhat by mechanically deforming the sample, which has the effect of generating at least partial alignment of the constituent polymer chains, thereby recovering some of the molecular anisotropy at a macroscopic level (McBrierty and Ward, 1968, 1971b; Ward, 1982; Nomura, 1989). This macroscopic anisotropy, which is revealed in a wide range of experimental NMR and other data, can be used to characterise the spatial distribution of molecules in deformed polymers as described in Chapter 7.

The principal ingredients of a model for a polymer are the following.

- The intrinsic response of the structural unit which, in the NMR context, requires information on the positions and motions of contributing nuclei.

- The relative amounts of distinguishable phases present since the macroscopic response involves contributions from the different phases. In many cases this information is contained in component intensities of resolved contributions to the NMR linewidth.
- In calculating the aggregate response of all the constituent structural units, account must be taken of their orientation relative to a chosen axis in the polymer sample, which in turn requires information on the statistical spatial distribution of units in the sample. Conversely, experimental NMR data for oriented polymers may be used to extract information on the distribution itself.

The practical implementation of these ideas will become evident in succeeding chapters. Where appropriate, the basic model is refined to take account of additional considerations such as distributions of correlation frequencies and/or the effects of spin diffusion.

1.4 Molecular motion: an overview

The sensitivity of NMR to molecular motion of appropriate frequency and amplitude underpins the usefulness and, on occasion, indispensability of the method in unravelling the complexities of molecular relaxation. An initial, somewhat general, consideration of molecular motion in polymers will help to clarify and put into perspective the analytical methodology and interpretations encountered in subsequent chapters.

Complexity arises in several ways.

- Cooperativity, anisotropy, and the effects of geometrical constraints are typical earmarks of molecular motion in polymers.
- Several discrete motions may be active simultaneously.
- Broad distributions of correlation frequencies, routinely encountered in practice, can only be dealt with semi-quantitatively.
- The complex motion of *internuclear* vectors generated from the *relative* motions of nuclei is difficult to deal with analytically other than in a few special cases.
- The way in which defects promote motion within their sphere of influence, particularly in polymers that are dilute in impurity defects, can be difficult to quantify.
- Both timescale *and* spatial dimension of the motion are important.
- Whereas the detection of specific molecular motions can be reasonably straightforward, the nature of the motional mechanism is often obscure.

Table 1.2. Typical motions observed in polymers

Motion	Region ^(a)	Nature	Typical activation energy (kJ mol ⁻¹)	Remarks
Primary main chain	C	Hindered rotations, oscillations or translations	> 125	May be activated by defects
Primary main chain	A	Large-scale rotations and translations	< 400	Associated with glass transition and breakdown of long-range order: ΔE is usually temperature-dependent
Secondary chain motion	C/A	Localised motion of interfacial material: cilia, folds, tie molecules, chains of low molecular weight	40–60	Characteristic of linear polymers: some or all chains may be involved
Sidegroup	C/A	Highly localised motion of specific moiety	8–80	Usually in the low-temperature regime below T_g
Impurity motions	C/A	Motions induced by trace solvents or low molecular weight material which can act as a plasticiser	—	Dominates relaxation at low temperature

^(a) C = crystalline; A = amorphous.

Much effort has been expended in seeking a better overall understanding of molecular motion in polymers. Many models based upon a range of fundamentally different premises have been developed, some principally to describe dielectric and dynamic mechanical relaxation while others have addressed the problem from the specific standpoint of NMR. Detailed comparison of a number of the more frequently used models has shown gratifying consistency (McBrierty and Douglass, 1980), which supports the contention that the approach adopted reasonably predicts the behaviour of real systems and that the correlation of diverse experimental data is not strongly model-dependent. Significant progress has also been achieved in computer generation of realistic polymer models (Spiess, 1983; Hirschinger *et al.*, 1990). At the microscopic level, multidimensional NMR is progressively removing the ambiguities implicit in molecular motional assignments. This is rather graphically illustrated for the α -relaxation in poly(vinylidene fluoride) as described in Section 5.4.5 (Hirschinger *et al.*, 1991).

Having placed the problem in context, procedurally it is usual to adopt a somewhat pragmatic interpretive approach whereby initially assumed idealised models for specific molecular motions are subsequently refined, intuitively or otherwise, to take account of the range of complexities discussed above. In the spirit of this approach, McCall (1969) classified molecular motion in polymers under a number of broad headings (table 1.2).

Generally, models which describe the Brownian motion of a chain of elements reasonably account for polymer behaviour in solution and can be extended in modified form to describe adequately the rubbery state (Cohen-Addad and Guillermo, 1984; Brereton, 1990). They are wholly inadequate when dealing with the glassy or crystalline states where more local motions involving activated motion over barriers between conformational isomers are encountered. In such cases one must resort to models that are based, for example, on the motion of defects, originally devised by Glarum (1960) and adapted subsequently by several groups. Unlike the defect diffusion model, the graphically appealing reptation model developed by Edwards (1967), de Gennes (1971, 1976) and Doi (1975) was designed specifically to describe polymer relaxation involving motion over long distances and times. This model visualises the random movement of defects along a polymer chain which is geometrically confined within a 'tube' whose axis assumes random coil conformation (fig. 1.4). In the polymer, the tube may be thought of in terms of the topological constraints imposed by neighbouring molecules.