Solid-State NMR Application Note: Organic Polymers

Introduction

Solid-state NMR is a powerful tool for the study of polymeric materials. Materials that are crystalline, semicrystalline, amorphous, homogeneous or heterogeneous, synthetic or natural can all be investigated. Presented here are some examples of the type of information that can be obtained using solid-state NMR.

Morphology and mobility

Solid-state NMR is particularly useful for probing the morphology of a material. Such information can be directly available in the $^{13}$C spectrum when crystalline and amorphous components have distinct chemical shifts, as is the case with polyethylene and cellulose. It is relatively straightforward to convert the observed intensity into a crystallinity value.

In the solid-state, $^1$H NMR usually gives little chemical information, but it can readily yield information on morphology. Crystalline and amorphous domains often exhibit different degrees of molecular motion and these impact on the $^1$H “wideline” spectrum (obtained from a non-spinning sample).

![Peaks from crystalline (c) and amorphous (a) domains are identifiable for polyethylene (left) and cellulose (right)](image)

In this “WISE” experiment on polyethylene the low-resolution $^1$H spectrum is correlated with a high-resolution carbon one (illustrated to the left).

![$^1$H relaxation curves showing a single component $T_1$ but two-component $T_{1p}$](image)

It is often the case that a sample has a single, common, $T_1$ value and that usually indicates that a sample is homogenous on a distance scale $>30$ nm. In contrast, multicomponent behaviour for $T_{1p}$ often indicates small-scale heterogeneity (on a scale of 5–30 nm) which is often missed by other analytical techniques such as thermal methods.
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Chemical identity

Unless its spectrum can be identified through the comparison of spectra from previously characterised materials, the determination of the chemical identity of an unknown substance by solid-state NMR is not straightforward. Nevertheless, some chemical information is readily available.

For example, it is possible to measure a degree of acetylation by comparing the intensity of acetyl signals to the other signals in the spectrum of chitin and cellulose acetate. The nature of sidechain branches in polyethylene are revealed in detail if high-resolution solid-state techniques (magic-angle spinning) can be applied to a softened sample (which sharpens the lines in the spectrum).

Combining techniques

It is common practice to obtain high-resolution $^{13}$C spectra from organic polymers using a technique called cross-polarisation. The carbon signal is generated by the transfer of magnetisation from the protons in the sample. This can be used to great advantage in complex, heterogeneous materials. With this technique the appearance of the carbon spectrum is strongly influenced by the relaxation behaviour of the protons. With knowledge of the proton relaxation behaviour, experiments can be designed to separately identify within a material: domains with a high degree of order, domains with high molecular mobility or rigid but disordered domains. In this way, the combination of relaxation measurements with high-resolution spectra can relate physical and chemical information.

More than just $^1$H and $^{13}$C

Solid-state NMR is not restricted to $^1$H and $^{13}$C. Fluorine NMR can provide useful information on fluorinated polymers. In poly(vinylidene difluoride), for example, amorphous and crystalline domains give distinct chemical shifts and defects in the polymer sequence can also be identified. Nitrogen-15 NMR is also a potential tool, although at natural abundance and with the broad lines typical of polymers, detectability can be an issue. However, adding a $^{15}$N label to a biopolymer can be quite straightforward and introduces another valuable investigative tool.

Durham Solid-state NMR Research Service

Durham University operates a Solid-state NMR Research Service for industry and on behalf of EPSRC. The Service is free to academic researchers in UK universities. The Service has a state-of-the-art, triple-channel 400 MHz spectrometer dedicated to service provision and has access to a range of other NMR instrumentation. We have equipment that can carry out all of the experiments illustrated here, including the specialist equipment for fluorine NMR. We also offer advice and training on the application of solid-state NMR.

If you would like to know more about our Service or more about solid-state NMR in general, visit our web site:

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