THE PHASES OF POLYMERS AS DETERMINED BY NMR

J. B. Miller

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375–5342, USA

Abstract

Nuclear magnetic resonance (NMR) spectroscopy has been used to study the morphology and dynamics in semicrystalline polymers. Dynamics may be observed through NMR relaxation rates that are sensitive to motions in the $1-10^8$ Hz range, or through modulation of anisotropic magnetic interactions, such as the chemical shift and dipole-dipole interactions. Morphological structure may be inferred through NMR measurements of polymer dynamics or investigated directly through studies of the magnetic interactions. Here, we discuss the study of morphological structure in semicrystalline polymers using NMR, and review results on poly(ethylene terephthalate) that address the question of the number of phases in this semicrystalline polymer.

Keywords: dynamics, morphology, semicrystalline polymers

Introduction

Nuclear magnetic resonance (NMR) spectroscopy [1, 2] is a tool familiar to most chemists for elucidating chemical structure in the liquid state. Chemical structure is derived from the chemical shift of the resonances from nuclei in different chemical environments. In liquids, the resonances are narrow, reflecting the average physical environment of the rapidly tumbling molecules. In solids, resonances are broadened by the distribution of physical environments in amorphous materials and by the chemical shift anisotropy with respect to the direction of the applied magnetic field. Magnetic dipole-dipole interactions between nuclei and the nuclear quadrupole interaction (for nuclear spins greater than 1/2) lead to additional broadening in solids.

Besides the spectral features of NMR several relaxation times characterize the nuclear spin system within the material. The two most important are the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2: T_1 characterizes the time required for the spin system to become polarized along the static magnetic field, i.e., to come to thermal equilibrium; T_2 characterizes the time spin phase coherence is maintained after the thermal equilibrium is disturbed. Other relaxation times may be defined by the particulars of a given NMR experiment.

NMR can be used for the analysis of phase morphology in polymers, and in particular, the determination of crystallinity. From the foregoing discussion, two principal methods become apparent: lineshape analysis and relaxation time measurements. Differences in relaxation times result from variations in the frequency and amplitude of molecular motions in different polymer domains. The various NMR

relaxation times are sensitive to different frequencies, generally within the range of $1-10^8$ Hz. Differences in lineshape can arise from variations in chemical/physical environment or, as with relaxation time measurements, from variations in the frequency and amplitude of molecular motions. Many examples of the use of NMR techniques to address the phase morphology of polymers can be found in the literature [3]. Below we discuss results on poly(ethylene terephthalate) (PET).

Discussion

The proton NMR spectrum of semi-crystalline polymers at temperatures between the glass transition and the crystal melting temperatures is characterized by superimposed broad and narrow resonances. Immobile polymer phases give rise to the dipolar broadened resonance; the motionally narrowed resonance is due to amorphous material above the glass transition. Proton NMR has been applied to the study of PET [4, 5] by fitting the wide line NMR signal measured above the glass transition temperature to a two-component function [4]. From the fit, the quantity of material associated with the broad component exceeds the degree of crystallinity found by other methods. This was ascribed [4] to the presence of taut amorphous chains that, like the crystalline material, do not exhibit motional narrowing. From the proton NMR data the extent of taut tie molecules in PET [6, 7] can be assessed. These structures exert an important role in determining the physical properties of the fibers.

Proton NMR relaxation time measurements can also be used to determine the phase structure of polymers below the glass transition. The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, has been used for investigating the degree of crystallinity in PET [8]. (The rotating frame refers to a rotating coordinate system where nuclear spin precession in the static magnetic field appears static. The $T_{1\rho}$ relaxation is the process of the spins coming into equilibrium along an applied *rf* field in this rotating frame.) Interpretation of these proton NMR relaxation times is confounded by spin diffusion [9], a process in which polarization gradients in regions of differing relaxation times are equilibrated by polarization exchange through the dipole-dipole interaction, leading to the observation of averaged line-shapes or relaxation times. The problem of spin diffusion can be overcome, however, by measuring $T_{1\rho}$ in a rotating frame where the dipole-dipole interaction is inoperative. (Details of these rotating or toggling frames are beyond the scope of this brief discussion. The interested reader is referred to the literature [10].) One such rotating frame (called a toggling frame in the multiple pulse cycle literature) is created in the MREV-8 pulse cycle [11]; the relaxation time in this particular rotating frame, known as T_{1xz} retains the $T_{1\rho}$ sensitivity to both the amplitude and frequency of motions. Because the T_{1xz} determination effectively quenches spin diffusion, it can distinguish between components of different mobilities, the contributions from which are smeared by spin diffusion in the other NMR experiments.

Havens and VanderHart [8] have made $T_{1\rho}$ and T_{1xz} measurements on various annealed PET fibers. They find that the $T_{1\rho}$ data can be fit with a two-exponential

function, whereas the T_{1xz} data requires at least three exponentials. The three time constants, in the order of longest to shortest, are assigned to crystalline, constrained amorphous, and amorphous phases, respectively. By measuring the rates of polarization exchange between phases, the authors can measure domain sizes, crystallite surface areas, and relative connectivities of domains. They find that all three domains are in contact with each other, ruling out the possibility that the constrained amorphous phase is an interfacial domain between crystalline and amorphous domains.

Roland et al.[12] also have performed T_{1xz} measurements on PET fibers and films. They find that crystallization occurs at the expense of oriented amorphous chains, but that there is no correlation between orientation and constrained amorphous content; annealing leads to a reduction in both amorphous phases and an increase in crystallinity, as also observed by Havens and VanderHart [8]. Roland et al. point out some limitations of determining crystallinity by other techniques and suggest NMR as a method for crystallinity determinations.

Lineshape analysis in ^{13}C NMR has been applied recently to the study of semicrystalline PET fibers [13, 14]. The ^{13}C experiments are performed with magic angle spinning and proton decoupling to allow the observation of isotropic chemical shifts [1]. As with proton NMR, the ^{13}C resonances can be resolved into broad and narrow components, with a small chemical shift difference between the components. In contrast to the proton NMR results, the ^{13}C NMR line associated with the crystalline fraction [13] is narrow, reflecting the high degree of order in the crystalline region. The amorphous fraction exhibits a resonance broadened by a distribution of chemical shifts associated with the disordered physical environment. Unlike the proton NMR lineshape that is determined by molecular dynamics, the ^{13}C NMR lineshape in PET is dominated by the effects of molecular ordering, allowing these measurements to be made below the glass transition.

All the ^{13}C NMR resonances are narrow compared with the proton resonances, allowing the observation of chemical shift differences between ethylene and carbonyl carbons. Tzou et al. [14] find that for all PET yarn samples studied, the linewidth ratio of narrow:broad resonance for the ethylene carbons is always equal to or greater than for the carbonyl carbons, implying a third polymer phase where the ethylene carbons are ordered but the carbonyl carbons are not. In addition, they find that the fraction of carbonyl carbons in the narrow resonance is always equal to or exceeds the degree of crystallinity as measured by non-NMR techniques. This is interpreted as a fourth, non-crystalline polymer phase where both ethylene and carbonyl carbons are in an ordered environment [14]. It is observed that annealing the yarns above the glass transition converts amorphous material to crystalline, with little change in the oriented amorphous components.

Gabriëlse et al.[15] have used ^{13}C $T_{1\rho}$ to investigate phase morphology in PET yarns. The ^{13}C $T_{1\rho}$ measurements do not suffer from the problem of spin diffusion because of the 1% natural abundance of ^{13}C nuclei. This experiment is interesting in that the $T_{1\rho}$'s can be measured for each resonance in the ^{13}C spectrum, correlating the molecular ordering with molecular dynamics. They find that a single $T_{1\rho}$

value can be assigned to the narrow ^{13}C resonances associated with the crystalline phases. However, the broad resonances of the amorphous material show a biexponential $T_{1\rho}$ decay. The finding of crystalline, amorphous, and rigid amorphous phases in PET agrees with the results of Havens and VanderHart [8]. The measurements of Gabriëlse et al. reveal the presence of amorphous and rigid amorphous material even in purely amorphous yarns, an observation also made by Havens and VanderHart [8], and Roland et al. [12]. From proton $T_{1\rho}$ measurements, the authors estimate crystalline domain sizes that agree well with X-ray results.

Conclusions

NMR techniques provide a powerful means of studying phase morphology in polymers. Morphology questions can be addressed from the point of view of molecular dynamics or molecular ordering using NMR. Furthermore, NMR experiments can be designed to correlate these two points of view. We have provided examples from the literature on the use of NMR to address phase morphology in PET. More than two distinct domains are detected by NMR in PET. Besides the crystalline and amorphous domains, a third domain is detected with molecular dynamics intermediate to the former two domains, and disordered like the amorphous phase.

*   *   *

References

1 R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Pitman, London 1983.
2 R. R. Ernst, G. Bodenhausen and A. Wokaun, "Principle of Nuclear Magnetic Resonance in One and Two Dimensions", Clarendon, Oxford 1987.
3 See for example: (a) R. Kitamaru, F. Horii and K. Murayama, Macromolecules, 19 (1986) 636; (b) S. Saito, Y. Moteki, M. Nakagawa, F. Horii and R. Kitamaru, Macromolecules, 23 (1990) 3256; (c) J. Clauss, K. Schmidt-Rohr, A. Adam, C. Boeffel and H. W. Spiess, Macromolecules, 25 (1992) 5208.
4 U. Eichhoff and H. G. Zachmann, Makromol. Chem., 147 (1971) 41.
5 A. Cunningham, A. J. Manuel and I. M. Ward, Polymer, 17 (1976) 126.
6 H. J. Biangardi and H. G. Zachmann, J. Poly. Sci. Poly. Sympos., 58 (1977) 169.
7 H. G. Zachmann, Poly. Eng. Sci., 19 (1979) 966.
8 J. R. Havens and D. L. VanderHart, Macromolecules, 18 (1985) 1663.
9 N. Bloembergen, Physica (Utrecht), 15 (1949) 385.
10 C. P. Slichter, "Principles of Magnetic Resonance", 2nd ed., Springer-Verlag, New York 1980.
11 (a) P. Mansfield, J. Phys. C, 4 (1971) 1444; (b) W.-K. Rhim, D. D. Elleman and R. W. Vaughan, J. Chem. Phys., 58 (1973) 1772; (c) W.-K. Rhim, D. D. Elleman and R. W. Vaughan, J. Chem. Phys., 59 (1973) 3740.
12 C. M. Roland, J. H. Walton and J. B. Miller, Magn. Reson. Chem., 32 (1994) S36.
13 M. D. Sefcik, J. Schaefer, E. O. Stejskal and R. A. McKay, Macromolecules, 13 (1980) 1132.
14 D. L. Tzou, P. Seai, A. S. Abhiraman and T.-H. Huang, J. Poly. Sci. Poly. Phys., 29 (1991) 49.
15 W. Gabriëlse, H. Angad Gaur, F. C. Feyen and W. S. Veeman, Macromolecules, 27 (1994) 5811.