

A solid-state ^{13}C NMR analysis of molecular dynamics in aramide polymers

Dan McElheny^a, Veronica Frydman^b, Lucio Frydman^{b,*}

^a*Division of Biological Sciences, University of Chicago, Chicago, IL 60637, USA*

^b*Faculty of Chemistry, Weizmann Institute of Sciences, 76100 Rehovot, Israel*

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Dedicated to Alex Pines in celebration of his 60th birthday

Abstract

The local dynamics of aromatic cores was analyzed for a homologous series of polyamides in the solid phase incorporating phenyl, biphenyl and naphthyl groups. Preliminary wide-line and spin-relaxation variable-temperature ^1H NMR measurements revealed the presence of thermally activated molecular motions for each polymer studied. A number of ^{13}C NMR experiments were then implemented to further clarify the nature and extent of such motions. These included ^1H – ^{13}C 2D separate-local-field measurements, whose line shapes revealed that motions involved for all cases a superposition of states. These could in principle be associated with rigid and mobile populations in these semi-crystalline aramides, a model that yielded a proper description of the spectra at all temperatures. To further probe this model the relaxation behavior of the aramides' ^{13}C spins was monitored in the rotating frame as a function of temperature, in both the presence and absence of homonuclear ^1H – ^1H decoupling. The variations observed in these measurements evidenced a thermally activated, relatively broad distribution of motional rates in the polymers. Editing the 2D local-field data according to the ^{13}C relaxation also supported this heterogeneous dynamic model. The mechanism underlying this behavior and implications towards the ^{13}C analysis of motions in aramides in particular and complex polymers in general, is briefly discussed.

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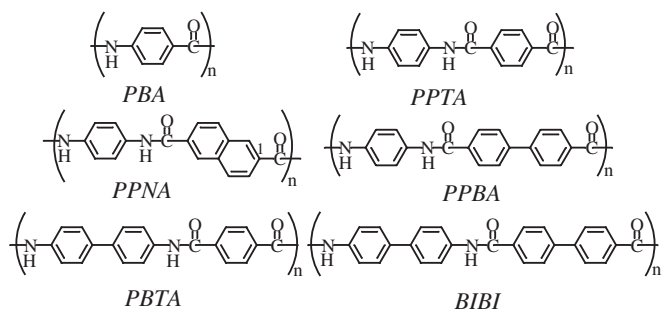
1. Introduction

The molecular dynamics of polymers in general and liquid crystalline polymers in particular, is known to deeply affect the tensile and impact properties of these materials [1,2]. Extensive efforts have been devoted to define the dynamic/mechanical relationships in such semi-crystalline macromolecules via a variety of means, of which NMR provides one of the most detailed molecular probes [3–5]. In this contribution we employ an assortment of natural abundance solid-state NMR techniques in order to study dynamics within the homologous series of aromatic polyamide (aramide) polymers illustrated in Scheme 1. The interest in the molecular dynamics of these liquid

crystalline polymers reflects the fact that such ultra-strong materials are utilized in the solid state [2,6,7]. The main constituent within this family of polymers is poly (*p*-phenylene)-terephthalamide (PPTA), which upon being spun from a liquid-crystalline solution serves as the basis for the Kevlar® brand of commercial fibers [8–10]. PPTA fibers have been analyzed by a wide variety of analytical techniques including solid-state NMR [11–16], and been shown to possess both crystalline and amorphous portions which exhibit significantly different dynamic behaviors. This kind of dynamic heterogeneity is best elucidated if a number of complementary spectroscopic approaches are used to measure the rates of motion encountered. We describe here the application of a variety of solid-state dynamic NMR approaches to the elucidation of motions in aramides, and make a critical evaluation of the potential and limitations encountered when applying such natural

*Corresponding author. Fax: +972 8 9344123.

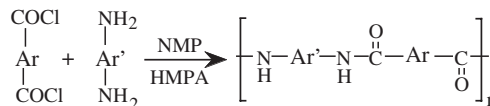
E-mail address: lucio.frydman@weizmann.ac.il (L. Frydman).



Scheme 1.

abundance NMR experiments to this kind of heterogeneous systems.

NMR has traditionally been used to analyze solid-state dynamics by relying on relaxation rate measurements, on line shape changes, and on multi-dimensional exchange correlations [3–5,17,18]. Each of these approaches is sensitive to dynamics over a particular range of timescales, defined by both the technique as well as by the type of interaction being monitored. For example measurements of spin-lattice relaxation T_1 are sensitive to correlation times $\tau_c \approx \omega_0^{-1} \leq 10^{-7}$ s, motions which are considered fast in solid-state environments. An intermediate dynamic regime with correlation times between 10^{-7} s $< \tau_c < 10^{-3}$ s can be monitored either through line shape changes from the dipolar or chemical shift anisotropies, or through rotating-frame relaxation ($T_{1\rho}$) measurements. The slowest of molecular dynamic processes can usually be followed with multi-dimensional exchange NMR measurements, which monitor correlation times up to the T_1 times of the nuclei being studied (in the order of seconds). As part of the present study we decided to focus on the first two of these regimes, in the hope of better defining the wide range of thermal processes potentially arising in aramides. Our main observable stemmed from fitting the line shape changes arising in aromatic ^1H – ^{13}C dipolar field spectra. Such line shapes are readily discerned in so-called two-dimensional separate-local-field magic-angle-spinning (2D SLF MAS) NMR [19–23], a family of techniques capable of revealing as sideband spectra the extent of the dynamics occurring for each isotropic site in a molecule. In the present work such data were measured and analyzed to extract information about the types of motions that might be occurring within the homologous aramide polymer series in Scheme 1. In an effort to better define the actual kinetic rates of the motions detected by the 2D SLF MAS NMR data, relaxation studies were also implemented. It was concluded that in the simplest of these sequences, involving $T_{1\rho}$ measurements, the processes driving the temperature-dependent spin relaxation did not arise solely from the molecular motions revealed by the SLF data. Because spin relaxation is widely used for quantitatively analyzing the rates of polymer dynamics, we considered it worthwhile contrasting the different pictures provided by the SLF and



Scheme 2.

the $T_{1\rho}$ relaxation data for each polymer. Further conclusions regarding aramide dynamics in particular and dynamic NMR in general, are described below.

2. Experimental

All the determinations described in the present study were carried out on polymer samples synthesized in our laboratory following guidelines described in patented procedures [24,25]. The main feature of these preparations are summarized in Scheme 2. All NMR measurements were carried out using laboratory-built multiple-resonance NMR spectrometers; the majority utilizing a 7.2 T Magnex magnet equipped with a commercial 4 mm Varian/Che-magnetics Pencil probe and variable-temperature accessories, and the remainder on a 11.75 T solids apparatus. For the 1D and 2D ^{13}C NMR acquisitions we used a ramped cross polarization centered at ≈ 50 kHz, ^1H decoupling at ≈ 100 kHz, and MAS at 10 kHz. Details for the specific kind of 2D SLF MAS acquisitions utilized in the present work, both in terms of their experimental setup, their processing and analysis, have been extensively discussed in Ref. [26].

3. Results and discussion

3.1. Dynamic dipolar line shape changes in aramides

Before attempting to quantify the potentially complex molecular dynamics occurring in the aramide series through 2D ^{13}C NMR experiments, we found it advantageous to test the overall presence of such dynamics via the acquisition of static ^1H NMR spectra. This in turn provides a simple and sensitivity route for probing molecular dynamics in the systems of interest, while yielding an approximate value of the point at which motions at rates comparable to the ^1H dipolar line width (≈ 50 kHz) activate [17,18]. Fig. 1 illustrates static 501 MHz ^1H NMR spectra recorded for the aramides, over a fairly wide ($>400^\circ\text{C}$) temperature range. The spectral changes observed are quite pronounced, attesting to the presence of dynamics in all members of the aramide family. Moreover, the dynamics seem to affect the ^1H line widths in a nearly continuous fashion as a function of temperature. This is by contrast to the more step-like changes usually found in molecular crystals, and is suggestive of a distribution of kinetic rates.

Having unambiguously defined the presence of molecular motions in the aramides' solid state, variable-temperature

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