

# A Weight-Averaged NMR Spin–Spin Relaxation Time Constant and Its Determination

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Proton magnetic resonance thermal analysis (PMRTA) has been proven to be a convenient yet powerful tool for detecting molecular mobility as a function of temperature for a hydrogen-containing organic and polymeric material (1–3). This technique essentially records the proton magnetic resonance ( $^1\text{H}$  NMR) spin–spin relaxation signal of a sample at various temperatures. The signal decays rapidly for rigidly bound molecules, but more slowly as molecular mobility is acquired, usually with an associated shift in signal shape from the exponential type to the Gaussian type.

A curve-fitting technique can be employed to obtain the relaxation time constants to quantitatively assess molecular mobility of a sample. However, it is a time-consuming process when a signal consists of more than two components (the exponential and Gaussian components) so that more than four variables (two intensities and two time constants) are involved, and no satisfactory unique fitting can be anticipated. Also four parameters rather than one make a comparison of the mobility difficult in practice.

This fact has led Lynch *et al.* (1–3) to develop a linearized truncated second-moment parameter to assess the molecular mobility of a material. In this approach, a time-domain relaxation signal is Fourier transformed to obtain the frequency spectrum of the signal, from which the moment parameter is computed at a certain truncation frequency ( $l$ ). Truncation of the frequency spectrum is necessary because the second moment for the exponential component in a relaxation signal diverges. However, this parameter, which decreases with increasing molecular mobility for a certain truncation frequency, is useful for practical purposes.

It will be shown in the following that the normalized signal area itself, i.e., the area encompassed by a relaxation signal and the intensity axis and zero line of the signal divided by the initial intensity of the signal, could be a quantitative measure of molecular mobility. It is clear from Fig. 1 that a slowly decaying signal will have a larger normalized signal area, and a rapidly decaying signal a smaller area. This phe-

nomenal observation can be verified by the following theoretical derivation.

Assuming that a relaxation signal consists of exponential and Gaussian components, one writes the signal,  $I(t)$ , as

$$I(t) = I_e^0 \exp\left(-\frac{t}{\tau_{2e}}\right) + I_g^0 \exp\left(-\frac{t^2}{(4/\pi)\tau_{2g}^2}\right), \quad [1]$$

where  $I_e^0$  and  $I_g^0$  are the initial signal intensities of the exponential and Gaussian components,  $\tau_{2e}$  and  $\tau_{2g}$  are the NMR spin–spin relaxation time constants of the exponential and Gaussian components, and  $t$  is the time. Note that the time constant in the Gaussian component is defined slightly differently from that in the literature, in which the time constant is defined to be either  $t^2/(2\tau_{2g}^2)$  or  $t^2/(\tau_{2g}^2)$  (4, 5).

Integrating Eq. [1] from  $t = 0$  to infinity results in the signal area,  $S$ , which in turn leads to the normalized signal area,  $s$ , by dividing  $S$  by the initial signal intensity,  $I^0$  ( $I^0 = I_e^0 + I_g^0$ ):

$$s = \frac{I_e^0}{I^0} \tau_{2e} + \frac{I_g^0}{I^0} \tau_{2g} = \bar{\tau}_2. \quad [2]$$

Equation [2] shows that the normalized signal area represents a weight-averaged relaxation time constant of the signal,  $\bar{\tau}_2$ , if the constant of the Gaussian component is defined according to Eq. [1]. Thus, this parameter should reflect a weight-averaged molecular mobility of a material examined.

A complicated relaxation signal resulting from a heterogeneous material may be very often found to consist of not only the exponential and Gaussian components but also other Weibull components. Yet a more complicated signal could also contain various subcomponents with different time constants for each component. Too many parameters actually invalidate the curve-fitting technique in practice.

Assuming that an NMR signal consists of  $N_c$  relaxation components and  $N_s(i)$  relaxation subcomponents for each component ( $i = 1, 2, \dots, N_c$ ), one writes the signal

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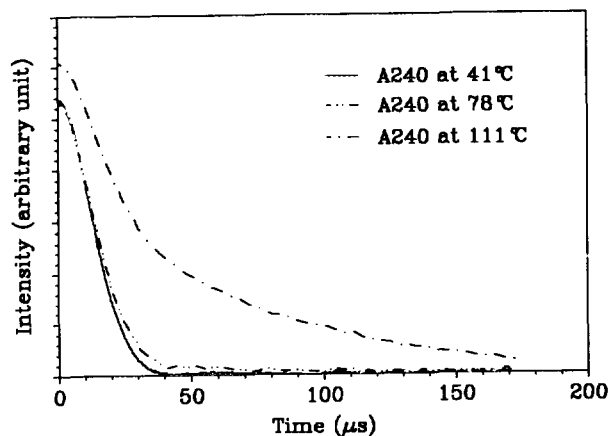


FIG. 1. Relaxation signals of A240 petroleum pitch at various temperatures.

$$I(t) = \sum_{i=1}^{N_c} \sum_{j=1}^{N_d(i)} I_{i,j}^0 \exp \left[ - \left( \frac{t}{\frac{\tau_{2i,j}}{\Gamma(1/n(i) + 1)}} \right)^{n(i)} \right] \quad [3]$$

$$I^0 = \sum_{i=1}^{N_c} \sum_{j=1}^{N_d(i)} I_{i,j}^0, \quad [4]$$

where  $I_{i,j}^0$  and  $\tau_{2i,j}$  represent the initial intensity and relaxation time constant of the signal for subcomponent  $j$  of component  $i$ , and  $n(i)$  is the Weibull function coefficient of component  $i$ . When  $n(i) = 1$  or  $n(i) = 2$ , the exponential or Gaussian component is obtained. The symbol  $\Gamma$  denotes the gamma function ( $\Gamma(2) = 1$ ,  $\Gamma^2(3/2) = \pi/4 \dots$ ).

Integrating Eq. [3] from  $t = 0$  to infinity and dividing the integrand by the total initial intensity,  $I^0$ , results in the normalized signal area (see Appendix):

$$s = \sum_{i=1}^{N_c} \sum_{j=1}^{N_d(i)} \frac{I_{i,j}^0}{I^0} \tau_{2i,j} = \bar{\tau}_2. \quad [5]$$

Equation [5] shows definitely that the normalized signal area is always equal to the weight-averaged relaxation time constant if the time constants in each of the relaxation components are defined according to Eq. [3].

A commercial-grade petroleum pitch (A240) of 125°C nominal Mettler softening point was employed for experimental demonstration. A pitch, consisting of a larger number of different polycyclic aromatic hydrocarbon molecules, is highly irregular and polydisperse in its chemical composition, molecular weight, and molecular structure, and therefore is a typical amorphous material.

About 600 mg of dried pitch was packed into a glass NMR tube. The PMRTA minispectrometer system used for the

measurements was equipped for temperature-regulated heating of the specimen and interfaced to a personal computer for system control and data acquisition, storage, and processing. The  $^1\text{H}$  NMR signals were recorded as a sample was warmed at 2°C/min from room temperature under a nitrogen atmosphere.

Figure 1 shows three NMR spin-spin relaxation signals of A240 at 41, 78, and 111°C. It can be seen from the figure that the signal area, and therefore the molecular mobility of the sample, increases at higher temperatures. By simply integrating the signals, one obtains the normalized signal area equal to the weight-averaged relaxation time constant, and hence the weight-averaged molecular mobility of the sample, as shown in Fig. 2.

The signal area kept a constant value around 15  $\mu\text{s}$ , and was seen to increase as the temperature rose above 60°C, which was the glass transition temperature of A240 according to the differential scanning calorimeter measurement, reflecting that the "frozen" molecular segments of the specimen acquired mobility above its glass temperature. The signal area showed further increase to around 1000  $\mu\text{s}$  as the temperature rose over 180°C. The specimen was completely fluid at these temperatures. It was also found that the value of 120  $\mu\text{s}$  can be used to determine the softening temperature of the specimen, so that a softening temperature consistent with the nominal value, which was determined using an ASTM method, could be obtained. This is to say that when the value of the weight-averaged time constant reaches 120  $\mu\text{s}$ , molecules of a specimen become so mobile that the specimen turns to a fluid from a solid at the softening point.

The normalized-signal-area parameter is simple in concept, and can be computed in real time as the signal is recorded. Another feature of this parameter is that high-frequency noise of a signal has little effect on the signal area

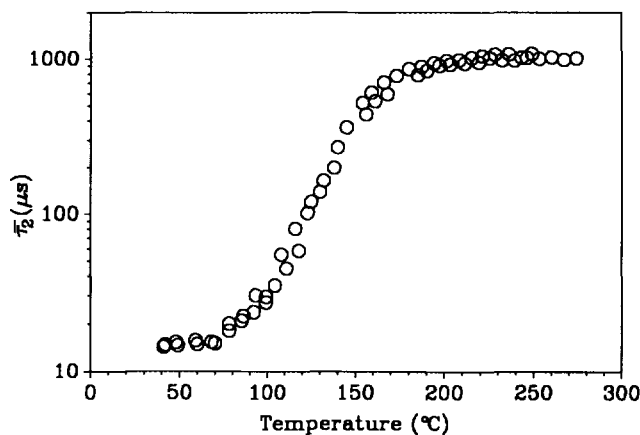


FIG. 2. Temperature variation of the weight-averaged time constant for A240.

since the noise will cancel on integrating the signal area, suggesting that no additional data treatment is required.

In conclusion, it has been found that the normalized signal area represents a weight-averaged spin-spin relaxation time constant which in turn represents the weight-averaged fluidity/molecular mobility of a material.

#### APPENDIX (6)

$$\begin{aligned} & \int_0^{\infty} I(t) dt \\ &= \int_0^{\infty} \sum_{i=1}^{N_c} \sum_{j=1}^{N_s(i)} I_{i,j}^0 \exp \left[ - \left( \frac{t}{\frac{\tau_{2i,j}}{\Gamma(1/n(i)+1)}} \right)^{n(i)} \right] dt \\ &= \sum_{i=1}^{N_c} \sum_{j=1}^{N_s(i)} \frac{\tau_{2i,j} I_{i,j}^0}{\Gamma(1/n(i)+1)} \frac{1}{n(i)} \int_0^{\infty} \exp(-u) u^{1/n(i)-1} du \\ &= \sum_{i=1}^{N_c} \sum_{j=1}^{N_s(i)} \frac{\tau_{2i,j} I_{i,j}^0}{\Gamma(1/n(i)+1)} \frac{1}{n(i)} \Gamma(1/n(i)) \end{aligned}$$

$$= \sum_{i=1}^{N_c} \sum_{j=1}^{N_s(i)} \frac{\tau_{2i,j} I_{i,j}^0}{\Gamma(1/n(i)+1)} \Gamma(1/n(i)+1)$$

$$= \sum_{i=1}^{N_c} \sum_{j=1}^{N_s(i)} I_{i,j}^0 \tau_{2i,j}$$

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