A Relationship between NMR Cross-Polarization Rates and Dynamic Storage Modulae of Polymers

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SYNOPSIS

A relationship between dynamic storage modulus (E') and the mean cross-polarization time constants $\langle T_{CH} \rangle$ for 16 polymer data sets has been established by using a standard linear solid model. This model is used in an attempt to equate the process of cross-polarization with mechanical rigidity by virtue of the implicit dependence of each phenomenon on molecular motion. The apparent validity of the relationship between these parameters indicates that cross-polarization in polymers can be a function of molecular motion in addition to microscopic spin dynamics. The limitations as well as practical applications of this relationship are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The use of cross-polarization (CP) between ^{1}H and ^{13}C nuclei has become a standard procedure for solid-state NMR studies of polymers.[1] More recent accounts have shown that the CP process is often heterogeneous under both Hartmann–Hahn match and mismatch conditions.[2-4] The higher sensitivity of inversion recovery methods has made it possible to experimentally observe multiple cross-polarizing components in organic materials.[2,5] This biexponential behavior has been attributed to several possibilities including proton reservoir heterogeneity at early stages during the CP process,[2-4] and phase heterogeneity.[5,6] In our studies, we have attempted to correlate average T_{CH} values with the modulus values of polymeric materials.[7,8] The partial success of these correlations implies that T_{CH} can also be influenced by molecular motions. Although this possibility has been qualitatively recognized, no definitive relationship between molecular motion and T_{CH} has been developed.

The CP process can be generally described by using thermodynamic arguments,[9-11] where the abundant proton or I spins are treated as an infinite homogeneous reservoir having a net positive spin temperature (most spins are aligned with the external magnetic field) and the rare carbon or S spins are treated as a small finite reservoir with a resultant small differential in energy level occupancy and, hence, a higher spin temperature. Prior to CP, the separation between carbon and proton energy levels are equalized in the "rotating frame" with the application of separate radio-frequency fields specific to each nucleus. Once this "Hartmann–Hahn" match is achieved, the "hot" carbon reservoir (rare S spins) is forced into thermal contact with the "cold" proton I reservoir, and the rare carbon S spins evolve to a new equilibrium at a spin temperature equal to that of the larger proton reservoir. This process results in a lower carbon spin temperature with proportionally more spins occupying the lower rotating frame Zeeman energy level. In turn, this results in an enhanced carbon signal intensity and is often necessary for achieving a high-resolution spectrum from a solid polymer.

The CP process is not instantaneous, but, instead, can be described as a process with a finite rate, T_{CH}, which is in competition with other relaxation processes such as carbon spin lattice relaxation in the rotating frame, $^C T_{1\rho}$, and proton spin diffusion processes that are often approximated by $^H T_{1\rho}$. At-

tempts have been made to quantify T_{CH} by using the general form of eq. (1):

$$1/T_{CH} = (1/2)(\sin^2 \theta_C)$$
$$\times (\sin^2 \theta_H)(M_2^{CH})[J(\Delta\omega)] \quad (1)$$

where θ_H and θ_C are the angles between the external field H_0 and the rotating frame fields of the respective nuclei; M_2^{CH}, the second moment of the heteronuclear dipolar coupling interaction (Van Vleck second moment); and J, a spectral density function that describes the modulation of the effective CP process by the degree of Hartmann–Hahn mismatch and by molecular motion.[12-14]

The power function J has often been approximated from a Fourier transform of an autocorrelation function C_x having a spatial dependence of $(1-3\cos^2\theta)/r^3$, with a Gaussian-type dependence on the dipolar fluctuation correlation time τ, and where C_x is divided by a normalizing term that has an angular spatial dependence like that of the second moment term M_2^{CH}. In the case of a rigid lattice with a strongly coupled proton reservoir, τ will tend to be short. In more mobile samples, molecular motion will tend to decrease the effectiveness of proton coupling, resulting in a longer τ (slower proton flip-flop rate). Although the motional dependence of CP has not been quantified, it can be qualitatively appreciated that the spatial dependence of the M_2^{CH} and C_x terms will be modulated by molecular motion, which, in turn, will modulate the rate of CP. To a first approximation, the normalizing term of C_x will cancel the angular spatial dependence (and, hence, the motion dependence) of the second moment term. However, even with this simplification, the angular spatial dependence of C_x is not completely eliminated.[14]

Given that the static component of the dipolar interaction is needed for efficient CP, it has been proposed that the process will be sensitive to near static, low-frequency molecular motions.[15] Although the effect of the motional correlation time τ_c on the dipolar fluctuation rate is difficult to quantify, the proton flip-flop rate will generally decrease (longer τ) with increasing rates of molecular motion (shorter τ_c). This implies that T_{CH} values are weighted by motional components with long correlation times where $1/T_{CH}$ scales with τ_c.

Despite the insufficient derivation of the motional dependence of T_{CH}, we have shown in previous studies that the average CP rate $\langle T_{CH} \rangle$ can be correlated with macroscopic mechanical properties like dynamic storage modulus or dynamic loss modu-

lus.[7,8] The existence of these types of correlations seems to support the idea that T_{CH}, E', and E'' are modulated by a similar distribution of correlation times. Our previous correlation was established with a combination of ideas that were taken from Maxwell and Maxwell–Weichert models. The average $\langle T_{CH} \rangle$ was taken from the weighted sum of multiple cross-polarized components and "domains" as defined from a biexponential IRCP fit accounting for competing ${}^H T_{1\rho}$ decay and from the stoichiometry of rigid and mobile domains as characterized by separate ${}^{13}C$ resonances (like the crystalline and amorphous peaks in polyethylene, and the aromatic and aliphatic domains in polyurethanes). The individual treatment of each component was analogous to the individual treatment of parallel Maxwell elements (springs and dashpots) that compose a Maxwell–Weichert model.[16,17] The average $\langle T_{CH} \rangle$ values were then incorporated into the more simplistic Maxwell model to develop a proportionality like that given by eq. (2), where $1/\langle T_{CH} \rangle \, \alpha \, \tau_c$:

$$E' \alpha [\omega^2 (1/\langle T_{CH} \rangle)^2]/[1 + \omega^2(1/\langle T_{CH} \rangle)^2] \quad (2)$$

Although these types of correlations show that T_{CH} can be related to macroscopic properties, their practical utility to date has been limited to small data sets of polymers. To expand the generality of the correlation between $\langle T_{CH} \rangle$ and E', we have combined the data generated from 16 polymer samples and we have replaced the simple Maxwell model with a standard linear solid model (SLS) as given by eq. (3)[16,17]:

$$E' = (E_g \omega^2 \tau_c^2 + E_r)/(1 + \omega^2 \tau_c^2) \quad (3)$$

where E_g is the glassy or unrelaxed modulus, and E_r, the rubbery plateau or relaxed modulus. Assuming that T_{CH} scales proportionally with τ_c, the SLS model enables us to define both a slope and intercept that improves the general utility of our correlation as given by eq. (4):

$$E' = (\omega c/\langle T_{CH} \rangle)^2(E_g - E') + E_r \quad (4)$$

where c is the defined proportionality constant between τ_c and T_{CH}, which is assumed to be linear in our simple model.

EXPERIMENTAL

Solid-state ${}^{13}C$-NMR data were acquired on a Bruker MSL-400 spectrometer operating at 100.627 MHz

carbon. In all cases, samples were run in ceramic rotors with magic angle spinning (54.7°) at a rate of 3–5 kHz. The Hartmann–Hahn match was established with an adamantane standard using a proton rf 90° pulse of sufficient strength and, hence, duration to also provide an effective proton decoupling frequency of 53–57 kHz during continuous data acquisition. All CP experiments were performed with recycle times of 2 s between experiments and with a signal averaging of 500–1000 scans per experiment.

The relative decay rates of ^{13}C magnetization through proton spin diffusion and spin lattice processes ($^H T_{1\rho}$) and the approximate contact time for maximum CP were determined from variable contact time experiments.[18] Apparent $^H T_{1\rho}$ values were obtained graphically from the inverse slope of plots of natural log intensity vs. contact time.

Inversion recovery cross-polarization experiments (IRCP)[5] were performed with initial contact times that were equivalent to the CP maxima from the variable CP experiments (typically 1.0–1.5 ms) and with contact times for 180° proton phase inversion that ranged from 10 μs to 8 ms. These relaxation experiments were also run at variable temperatures using a Bruker temperature control unit, with dry nitrogen for establishing subambient bearing and drive pressures.

The IRCP data (relative carbon intensity vs. inversion contact time) were then fit to a biexponential model accounting for competitive $^H T_{1\rho}$ decay processes.[6] The fit was typically achieved by using data from inversion contact times between 10 and 1000 μs. The biexponential T_{CH} constants for backbone polymer carbons were then multiplied by their respective weighting factors from the fitting process to calculate mean $\langle T_{CH} \rangle$ values.[7,8] In cases where

Table I Polymer Materials and Sources

Polymer	Source
L100 PU, polyurethane	Uniroyal
L167 PU, polyurethane	Uniroyal
EPU, polyurethane	Uniroyal
PS, polystyrene, Styron	Dow
PPO, poly(phenylene oxide)	Aldrich
PVF, poly(vinyl formal)	Polysciences
PVB/DHA, poly(vinyl butyral), plasticized	Monsanto
PVB, poly(vinyl butyral), DHA extracted	Monsanto
LDPE, low dens. polyethylene	Dow
PVC/DOP, poly(vinyl chloride), plasticized	Unknown

Table II Storage Modulus Values (E', at 1 Hz), Average CP Rates ($\langle T_{CH} \rangle$), and Respective ^{13}C Chemical Shifts That Were Used for Weighted Averaging

Sample	T (°C)	E' (Pa)	Chemical Shift (ppm)	$\langle T_{CH} \rangle$ (μs)
L100 PU	23	7.08×10^7	27, 136	2180
L167 PU	23	1.36×10^8	27, 130	2118
L167 PU	−20	6.61×10^8	27, 130	966
EPU	23	1.51×10^8	27, 33	2587
EPU	0	1.84×10^8	27, 33	1398
EPU	−15	2.29×10^8	27, 33	1237
PS	23	2.51×10^9	41	180
PPO	23	5.28×10^8	117	830
PVF	23	3.98×10^9	94	163
PVB/DHA	23	3.98×10^8	102	265
PVB/DHA	−20	1.41×10^9	102	233
PVB	23	1.86×10^9	102	194
PVB	−20	2.73×10^9	102	213
LDPE	23	6.31×10^8	31, 33	660
PVC/DOP	23	3.02×10^8	47, 58	434
PVC/DOP	−20	1.07×10^9	47, 58	279

phase separation is characterized by multiple backbone carbon resonances as with polyethylene and polyurethanes, T_{CH} values were weighted to account for the stoichiometric concentration of these phase domains as in previous studies.[7,8]

A list of samples and sources where applicable are given in Table I, while chemical shifts, E' values, and $\langle T_{CH} \rangle$ values are given in Table II. The polyurethane samples were prepared by reacting liquid prepolymers from Uniroyal Chemical Co. with a chain extender: either a diamine chain extender, 4,4'-methylene-bis-2-chloroaniline (MOCA), where the prepolymer was a poly(tetramethylene ether glycol) (PTMO) segment that was end-capped with toluene diisocyanate as in the L-100 and L-167 cases, or with a cyclohexyldithenol chain extender where the prepolymer was a PTMO segment that was end-capped with cyclohexyldiisocyanate as in the EPU cases.

Dynamic mechanical storage modulus data were obtained from either a TA Instruments 983-DMA or a Polymer Laboratories DMTA at a fixed frequency of 1 Hz. When samples were not obtained in film form, plaques were pressed at elevated temperatures using a Carver press. Correlations between $\langle T_{CH} \rangle$ and E' were established with eq. (4) using a fixed value of 10^{11} Pa for the unrelaxed glassy modulus and 1 Hz for the measurement frequency, ω.

RESULTS AND DISCUSSION

The general relationship between E' and $1/\langle T_{CH} \rangle$ is illustrated in Figure 1 using the data presented in Table II. The dependence of E' on $1/\langle T_{CH} \rangle$ indicates that $1/\langle T_{CH} \rangle$ may scale linearly with τ_c to a first approximation. Figure 1 shows that the relationship E' and $1/\langle T_{CH} \rangle$ yields an apparent plateau region and a transition region; however, there is no evidence of an unrelaxed glassy region as would otherwise be expected at long values of τ_c (at short values of $\langle T_{CH} \rangle$).

The assumption of linearity between T_{CH} and τ_c implies that T_{CH} can be either infinitely long or short depending on motional dynamics. Although this assumption appears valid in the plateau and transition regions, the absence of a clearly defined glassy region suggests that this assumption is too simplistic. This is likely due to the observation that T_{CH} will approach a lower limiting value that is characteristic of the spin dynamics in a rigid lattice environment.[13] Thus, at some level of "rigidity," molecular motion will probably not influence T_{CH}.

Although the true relationship between T_{CH} and τ_c is probably more complex, we have used the linear approximation to develop a correlation between $\langle T_{CH} \rangle$ and E' as shown in Figure 2 using the SLS model of eq. (4). Despite its limitations, this model provides an improvement over our previous correlations since it allows us to define a function of more practical utility. The correlation coefficient of .93 from regression analysis indicates that the trend is valid, but the model needs improvement.

Several simplifying assumptions have probably affected the quality of fit. For example, we have assumed that all the polymers are characterized by identical values for relaxed and unrelaxed modulae,
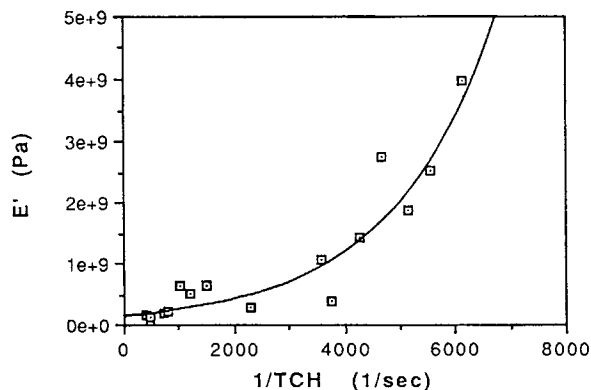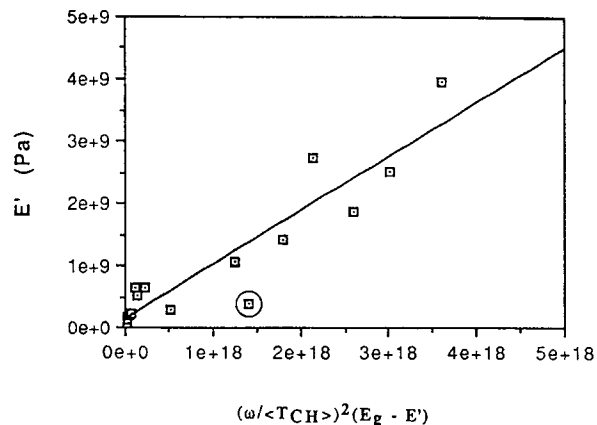
Figure 2 Correlation between E' (Pa) and $1/\langle T_{CH} \rangle$ (s^{-1}) using the standard linear solid model of eq. (4). $R^2 = 0.93$; $c = 2.95 \times 10^{-5}$ s^2; $E_r = 1.27 \times 10^8$ Pa.

E_r and E_g, respectively. This simplification is probably only valid when correlating a homologous series of polymers with similar structures such as polyurethanes with controlled midblock molecular weights and/or controlled end-block stoichiometries.

Also, samples with extreme mobility may have "domains" that do not cross-polarize. This would result in an inappropriate weighting of the biexponential T_{CH} values and, hence, a poor approximation of $\langle T_{CH} \rangle$. In our previous work, we accounted for noncross-polarizing mobile components by estimating their weight fractions.[7,8] However, with the exception of the plasticized PVB sample at room temperature, the present correlation is established with samples that qualitatively appear to completely cross-polarize. The criteria for this qualitative assumption would be longer $HT_{1\rho}$ values and a minimal change in the CP maximum intensity as a function of temperature. The data point for plasticized PVB is circled in Figure 2 to illustrate the skewing affect that it has on the correlation.

The slope of this correlation provides the proportionality constant ($c = 2.95 \times 10^{-5}$ s^2) between $1/\langle T_{CH} \rangle$ and τ_c and more generally may relate to the proportionality between $1/T_{CH}$ and $J(\Delta\omega)$ as seen from eq. (1). The intercept ($E_r = 1.27 \times 10^8$ Pa) seems to provide a reasonable estimate of the rubbery plateau modulus for a typical polymer.[17]

Assuming that eq. (1) holds, M_2^{CH} takes an approximate value (from $1/c$) of 6.8×10^4 s^{-2}, which is considerably smaller than the rigid lattice value of 2.5×10^8 s^{-2} (10^{10} rad^2/s^2) for a polyethylene carbon with two directly bonded protons.[13] Aside from the limitations of the SLS model, this discrep-

Figure 1 General relationship between E' (Pa) and $1/\langle T_{CH} \rangle$ (s^{-1}).

ancy is most likely related to the insufficient development of the relationship between T_{CH} and τ_c. Our calculated value may actually represent a hybrid of the rigid lattice second moment that has been modulated by some function of τ_c.

The fact that a general trend can be established between E' and $\langle T_{CH} \rangle$ indicates that T_{CH} can be modulated by molecular motion. Although no theory has been developed that adequately accounts for this modulation, our correlation shows that the potential for theory development exists. In addition to theory, more experimental data will be needed to determine frequency and temperature effects. For example, a controlled temperature study may be used to determine if $\langle T_{CH} \rangle$ follows a WLF type of temperature dependence above T_g. A study of this type could provide a better empirical framework for theory development.

Despite these limitations, our current correlation can have some applied utility in its present form. For example, this correlation makes it possible to approximate the "effective" modulus of the organic components in a polymer/inorganic composite using data from solid-state NMR. This capability would make it possible to determine the contribution of the organic phase to the bulk composite modulus. It should also be possible to more directly determine the effects of inorganic surface treatments on polymer phase mobility. This would be particularly desirable in applications where the inorganic/polymer composite surface interactions are thought to restrict or enhance the mobility of the polymer molecules.

It should also be possible to correlate T_{CH} with other motionally dependent properties such as viscosity in high solids suspensions. Such correlations could potentially make it possible to determine the effect of particle surface chemistry and solids loading on polymer and solvent phase mobilities. This could help with the development of models that attempt to predict the viscosity behavior of high solids ceramic slurries and organic coatings.

However, when quantitative trends are desired, it would be prudent to develop a correlation that is specific to a homologous series of polymeric materials. This may lead to the use of other carbon centers in addition to simple main chain carbons, and

it may help to minimize the variability in the nonmotional contributions to T_{CH} that arise primarily from spin–spin interactions and inhomogeneities in the proton reservoir.

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