

## **SOLID STATE NMR OF POLYMERS: A REVIEW OF MOLECULAR MOTIONS AND MORPHOLOGY**

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§ “...*The chest gave off a glacial exhalation. Inside there was only an enormous, transparent block with infinite eternal needles in which the light of the sunset was broken up into colorful stars...*”  
~Gabriel García Márquez

### 1.1 INTRODUCTION

The quest for understanding the relationships between physical properties and molecular motions in solid polymers has piqued the interest of scientists since the founding of polymer science (1,2,3). In the 1940's, Paul Flory began to apply statistical mechanics to the problem of determining the preferential configurations of polymer chains in liquid solutions (1). It was soon realized that the same arguments could be applied to polymer chains in the solid state. Flory's application of thermodynamics led to the currently accepted static model of a randomly coiled polymer chain, where the lowest energy chain-configuration (characterized by a unique end-to-end distance and radius of gyration) is determined by several structural considerations, including bond angles, bond distances, and bond rotational energy barriers. Although his model was static, it can be appreciated that polymer chains are anything but static. In fact, the dynamic or motional characteristics of polymer chains are governed by the energy levels that separate the various configurational states.

Despite the elaborate attempts by physical chemists to understand the

molecular origins of solid-state polymer properties, all quantitative theories have been limited to describing generalized and idealized behavior. As examples, the theory of simple rubber elasticity (a solid-state theory), and Flory's initial approximations of polymer configurations in solutions, both fail to embrace the importance of "long-range" interactions and their relationships to polymer properties. Moreover, long-range interactions often lead to complex morphologies in the solid state that further complicate any attempts to quantify and generalize polymer behavior (2).

To make matters worse, the methods used to study polymers in the solid state have been traditionally limited to bulk mechanical techniques, from which molecular characteristics are indirectly inferred. These techniques include mechanical measurements of creep and stress relaxation, measurements of impact resistance and other ultimate properties, and measurements of dynamic mechanical and dielectric properties as functions of temperature and rate (3).

Only with the advent of methods such as neutron scattering and solid state nuclear magnetic resonance (NMR) have scientists been able to directly probe the molecular characteristics of polymers in the solid state. However, the potentials of these techniques remain largely untapped; at this point, the relationships among molecular motions, morphology, and physical properties are still qualitative at best.

The purpose of this paper is to review the applications of one of these methods for studying molecular motion - solid state NMR. The relatively untapped potential of solid state NMR cannot be overstated. Specifically, this paper focuses on the applications of "vintage" NMR relaxation techniques that were developed in the 1970's and 1980's. Although simple by modern standards, these techniques continue to provide invaluable information to scientists who seek to understand the relationships among molecular motions, polymer morphology, and macroscopic properties.

## 1.2 SOLID STATE NMR: AN HISTORICAL INTRODUCTION

§ *"Many years later, as he faced the firing squad, Colonel Aureliano*

*Buendía was to remember that distant afternoon when his father took him to discover ice....*

*At that time Macondo was a village of twenty adobe houses, built on the bank of a river of clear water that ran along a bed of polished stones, which were white and enormous, like prehistoric eggs. The world was so recent that many things lacked names, and in order to indicate them it was necessary to point. Every year during the month of March a family of ragged gypsies would set up their tents near the village, and with a great uproar of pipes and kettledrums they would display new inventions....*

*Disconcerted, José Arcadio Buendía ventured a murmur: "It's the largest diamond in the world."*

*"No," the gypsy countered. "It's ice."*

*...Intoxicated by the evidence of the miracle...and with his hand on the cake, as if giving testimony on the holy scriptures, he exclaimed:*

*"This is the great invention of our time."*

Since the early 1940's, NMR has proven to be a valuable tool for studying molecular motions in solid materials. The world of the 1940's was no longer so "recent" as that of the Colonel Buendía in Marquez's famous story, yet Bloembergen, Purcell and Pound (4) were bound to relive their own versions of the Colonel's captivating discovery. They were to be among the first to use NMR relaxation techniques to elucidate the temperature dependence of molecular motions in solid ice (4). Exactly so "new" and thrilling must have been the moment when the three "rediscovered" ice!

They were undoubtedly captivated by the appearance of that first broad-line proton resonance (a featureless "bump" by today's standards). They must have been even more intrigued when they discovered that the ice's proton signal decayed with a temperature-dependent relaxation rate. Importantly, they explained this phenomenon with a theory that accounts for the effects of thermal motion on the lifetime of nuclear spin states - a theory that remains applicable even to this day.

Throughout the 1950's and 1960's, researchers in the field of solid state NMR were mostly concerned with advancing the techniques. In time, these

techniques would be used for the purpose of obtaining information about molecular motions. However, most of the early experiments were focused around the featureless decay and broadening of wide-line proton spectra (5).

It was not until the late 1970's, with the advent of cross polarization and magic angle spinning (CPMAS), that Schaefer et al. were able to demonstrate the utility of  $^{13}\text{C}$  NMR for studying molecular motions in solid polymers (6,7). Shortly thereafter, Schaefer and coworkers were the first researchers to attempt to relate NMR/molecular motion data to mechanical properties (8).

The purpose of the following discussions will be to provide a synopsis of "vintage" solid state NMR techniques that are particularly useful for elucidating information about molecular motions and morphology. Some of the most useful NMR techniques for this purpose include the temperature- and frequency- dependent measurements of  $T_1$  spin lattice relaxation, measurements of  $T_{1\rho}$  spin lattice relaxation in the rotating frame, measurements involving deuterium and  $^{13}\text{C}$  line broadening, and measurements involving proton-to-carbon cross polarization.

### 1.3 NMR – GENERAL BACKGROUND

§ "...he left the daguerreotype laboratory to the fantasies of José Arcadia Buendía, who had resolved to use it to obtain scientific proof of the existence of God.... He would stay up until very late, ...scribbling.... One night he thought he had found a prediction of the future of Macondo. It was to be a luminous city with great glass houses where there was no trace remaining of the race of the Buendías. "It's a mistake," José Arcadia Buendía thundered. "They won't be houses of glass but of ice, as I dreamed, and there will always be a Buendía, per omnia secula seculorum."

During an NMR experiment, nuclei with spin quantum numbers that are non-zero will experience a perturbation from the application of a static magnetic field. In the study of  $^{13}\text{C}$  nuclei (and other spin 1/2 nuclei such as  $^{31}\text{P}$  and  $^1\text{H}$ ), the degeneracy of nuclear spins will be lifted by the static field to yield two separate spin states of +/- 1/2. Most of the nuclei will reside in the lower energy spin state

(aligned with the external static field), while a smaller number of nuclei will reside in the higher energy state (aligned against the external static field). The distribution of spins between these energy states will be governed by a Boltzmann relation, with the relative populations depending on the energy-separation between the states (the energy-separation scales with the strength of the external static field).

The nuclear spins will also precess about the external field at a frequency that is proportional to the field strength (sometimes referred to as the Larmor frequency). A resonance condition can be achieved when a radio frequency field (rf) is applied perpendicular to the static field at a frequency that matches the Larmor frequency of the precessing nuclei. Under this condition, the static-field Boltzmann distribution is disrupted, and an additional fraction of lower energy spins will be excited to the higher energy spin state (it is important to note that the radio frequency field must be of low amplitude to prevent saturation of the nuclei among the energy levels, since such a condition would lead to a loss of signal intensity) (9,10).

When the rf field is removed, the nuclei will eventually "relax" to their previous equilibrium states. This relaxation process is defined as spin lattice relaxation, and is measured by monitoring the time-dependent decay of the magnetization, parallel to the axis of the external field (a  $T_1$ -type process). Generally, any process in the surrounding lattice which gives rise to localized fluctuating fields will eventually relax higher energy spins to lower energy spin states. The spin lattice process of nuclear relaxation does not involve the direct emission of a photon, but it can be thought of as a classical exchange of energy between nuclear dipoles and their surrounding environments, eventually leading to the relaxation of spins to their lower energy states through the dissipation of heat into the lattice (9).

Local fields can be generated by dipole-dipole interactions (DD – 40 kHz), electric quadrupolar interactions (200 kHz), chemical shift anisotropy interactions

(CSA – 50 kHz), scalar coupling interactions (3 kHz), and spin rotation interactions (0.1 kHz). These fields will fluctuate due to molecular motions in the lattice, and will give rise to spin lattice relaxation pathways for higher energy nuclei. It follows therefore that the rate, or efficiency, of spin lattice relaxation can yield direct information about the motional characteristics of molecules in both solids and liquids. The DD and CSA mechanisms are the most dominant and important relaxation mechanisms for nuclei with spin quantum numbers of  $I = 1/2$ , as is often the case for solid polymers.

During a spin lattice process, the nucleus can be imagined as a stationary object whose orientation with respect to an external field is controlled by the movement of the substrate that contains it (a molecular residue), or by the motion of adjacent nuclei, which induce reorientations by magnetic interactions. Again, this process ultimately results in the relaxing of higher energy spins to a lower energy spin state. Thus, the process is most efficient when the molecular motion has frequency components that match the Larmor frequencies of the processing nuclei.

The decay and broadening of an NMR band is largely controlled by the rate of local field fluctuations, which are induced by molecular motions (leading to spin lattice relaxation). However, there is another line-broadening mechanism that is not related to the degree of field fluctuation. This second relaxation pathway, known as spin-spin relaxation, is measured by monitoring the rate of magnetization decay that occurs in a direction that is transverse to the external magnetic field (a  $T_2$ -type process). When two spins are given sufficient contact time (as would be the case in a static frame of reference), spin information can be transferred by a spin flip-flop process with no net loss of energy. Thus, during spin-spin relaxations, the spin "information" is randomized throughout the lattice by continuous photon emission and re-absorption, with no accompanying net relaxation of spins to lower energy levels (5, 10). This process is most efficient in rigid systems.

Both the spin-spin and spin lattice processes will contribute to the overall relaxation of an NMR signal. However, the relative contribution of each will depend on the motional characteristics of the material and on the imposed set of experimental conditions. Thus, experiments can be designed to yield information about both processes – leading to information about molecular dynamics.

#### 1.4 SPIN LATTICE RELAXATION AND MOLECULAR MOTIONS ( $T_1$ )

§ *“Aureliano did not leave Melquiades’ room for a long time. He learned by heart the fantastic legends of the crumbling books, the synthesis of the studies of Hermann the Cripple, the notes on the science of demonology, the keys to the philosopher’s stone, the Centuries of Nostradamus and his research concerning the plague, so that he reached adolescence without knowing a thing about his own time but with the basic knowledge of a medieval man.”*

$T_1$  spin lattice relaxation times are sensitive to motions that fall into the frequency regime of the spectrometer (MHz region). This makes  $T_1$  experiments particularly important for elucidating localized motions that provide information about stereochemical and morphological differences among materials. Such information can ultimately lead to a better understanding of the relationships between polymer superstructure and mechanical properties.

Depending on the type of spectrometer and the nucleus being studied, the motional frequencies of importance can range from 60 to more than 600 MHz (5). This makes  $T_1$  values particularly sensitive to high-frequency side chain motions, as was found by Edzes and Veeman (11) in their studies of the effects of plasticizers and tacticity on the spin lattice relaxation of carbon nuclei in solid poly(methyl methacrylate) (PMMA).

They found that the MHz regime relaxation rates ( $T_1$ 's) for PMMA main-chain carbons are largely controlled by the motional reorientation rate of the  $\alpha$ -CH<sub>3</sub> methyl group. This conclusion was in part based on the observation that the relaxation times for neighboring carbon nuclei appeared to follow a  $1/r^6$  dependence (where  $r$  is the distance between the  $\alpha$ -CH<sub>3</sub> protons and the carbon

center of interest). They also noted that the relaxation rate for the isotactic methyl carbon was slower than that of the syndiotactic methyl carbon. Furthermore, the relaxation rates of the isotactic and syndiotactic main-chain carbons appeared to scale proportionally with the relaxation rates of each respective  $\alpha$ -CH<sub>3</sub> carbon. They attributed the differences in isotactic and syndiotactic T<sub>1</sub>'s to a tacticity-dependent difference in methyl group molecular mobility, where the  $\alpha$ -CH<sub>3</sub> is more mobile and less sterically hindered in the isotactic conformation (12).

Flemming et al. (14) observed that  $\alpha$ -CH<sub>3</sub> motional broadening prevents the measurement of the true T<sub>1</sub> minimum for the main-chain carbons of polypropylene. They noted that the methyl resonances for polypropylene, polycarbonates, PMMA, and epoxy polymers all undergo line broadening at temperatures where the methyl reorientation frequency (kHz range) is coincident with the proton dipolar decoupling frequency (note that high power proton decoupling - typically in the range of 50 to 100 kHz - is used during signal acquisition in solid state experiments).

By contrast, Gabrys et al. (15) have shown that  $\alpha$ -CH<sub>3</sub> motional broadening does not interfere with the measurements of T<sub>1</sub> minima for isotactic and syndiotactic PMMA's (i.e., there are no  $\alpha$ -CH<sub>3</sub> molecular motions with frequency components that are comparable to the kHz-range dipolar decoupling field - at least none within the temperature range of the T<sub>1</sub> minima). Like Edzes and Veeman (11), they attributed the differences in isotactic and syndiotactic T<sub>1</sub>'s to differences in  $\alpha$ -CH<sub>3</sub> molecular mobility (in the MHz range). This argument was supported by the observation that the i-PMMA T<sub>1</sub> minimum occurs at a lower temperature than the T<sub>1</sub> minimum for s-PMMA (15).

Interestingly, the sensitivity of localized  $\alpha$ -CH<sub>3</sub> motion to tacticity has proven to be beneficial in studies of polymer blends. For example, differences in T<sub>1</sub> relaxation rates among  $\alpha$ -CH<sub>3</sub> groups were used to study the morphological characteristics of isotactic and syndiotactic PMMA blends (15). Multi-component, bi-exponential T<sub>1</sub> relaxation times were observed for several blends



over a range of compositions. The  $T_1$  values were resolved to show the presence of separate morphological domains, comprising isotactic PMMA and syndiotactic PMMA. In addition, a third component was also observed with a  $T_1$  value that differed from the  $T_1$ 's of either neat polymer. This component was attributed to a 1/2 iso/syn-PMMA complex, which exists as a separate morphological domain, and represents an intimate molecular level blend of the two chain conformations. Thus, solid state NMR has the potential to elucidate morphologies based on differences in relaxation rates among separate phases.

In another account, Koenig et al. (16) used  $T_1$  spin lattice relaxation times to characterize the motional differences between the alpha and beta (strained) phases of poly(butylene terephthalate) (PBT). Upon stretching the polymer, the  $T_1$ 's for the non-protonated aromatic carbons were observed to decrease. This phenomenon was attributed to an increase in localized molecular mobility, an observation consistent with the fact that the unit cell of the beta phase is larger than that of the alpha phase (note that higher free volume is synonymous with increased molecular motion). The authors also pointed out that  $T_1$  relaxation times are relatively easy to interpret for two reasons: 1) spin-spin contributions to  $T_1$  are insignificant, which means that  $T_1$  relaxation is predominantly influenced by spin-lattice or motional processes; and 2)  $T_1$  values are relatively insensitive to decoupling field strengths.

Schaefer et al. (17) have shown that  $T_1$  values can be used to study the effects of thermal history on molecular motion in solid polymers. For example, when PBT was thermally annealed, the  $T_1$  values of the non-protonated aromatic carbons were observed to increase. This was attributed to a decrease in molecular mobility due to a reduction in free volume. Conversely, when the polymer was quench-cooled, the  $T_1$  values were observed to decrease, presumably due to an increase in free volume. These results imply that solid state NMR can be quite useful for studying the effects of polymer process history and physical aging on physical properties.

Schilling et al. (18) used  $T_1$  relaxation times to study the dynamic characteristics of a solid-solid phase transition that occurs in the crystalline domains of trans-poly(butadiene) (TPBD). They observed that the  $T_1$ 's of the amorphous domains remain relatively unaffected by the transition. In addition, they noted that upon selective epoxidation of the amorphous phase, the temperature and motional character of the crystalline phase transition was not affected. Thus, they concluded that the MHz-range motional characteristics of the amorphous phase are independent of the motional characteristics of the crystalline phase.

Aside from being used to study neat polymers and polymer blends,  $T_1$  relaxation experiments have also been successfully used to study plasticized systems. For example, Edzes and Veeman (11) have shown that in certain systems, plasticizer seems to have no effect on the MHz regime relaxation rates of main-chain carbons. Schaefer et al. (13) found similar results for the main-chain carbons of poly(vinyl butyral-co-vinyl alcohol) (PVB) (plasticized with various levels of dihexyladipate (DHA)). Both research groups used these results to suggest that plasticizers tend to enhance lower frequency motions (kHz-range and lower), and have little to no effect on the localized MHz-range motions that control the  $T_1$  spin lattice relaxation process. Indeed, this was supported by  $T_{1\rho}$  measurements made by Ritchey on PMMA (5), and by Schaefer et al. on PVB (13). ( $T_{1\rho}$  measurements are sensitive to motions in the kHz regime, as will be discussed in the  $T_{1\rho}$  section.)

By contrast, Parker et al. (19) have shown that plasticizer can sometimes have an “antiplasticization” effect on certain MHz regime motional processes. Variable temperature  $T_1$  experiments on PVB revealed that the  $T_1$  minimum for the PVB methyl side-chain (at 15 ppm) is shifted to a higher temperature in the presence of DHA. This shift was also accompanied by a decrease in glassy-state free volume (20), and by an increase in the activation energy for a glassy state  $\beta$ -transition (as measured via dynamic mechanical experiments) (19,20). The

activation energy for the PVB methyl-group motion was found to be  $2.7 \pm 0.2$  kcal/mol, independent of the presence of plasticizer, which shows that the character of the methyl group motion (likely to be a rotation) remains unchanged in the presence of DHA. However, the Arrhenius prefactor was observed to decrease, which shows that although the character of the motion remains unchanged, its frequency of occurrence decreases in the presence of plasticizer.

$T_1$  measurements have also been used to study the motional dynamics of solvents and polymers in heterogeneous suspensions. For example, spin-lattice ( $T_1$ ) and transverse relaxation ( $T_2$ ) techniques have been used to study liquid diffusion in emulsion droplets (21), and to study solvent mobility in polymer solutions. These techniques have also been used to study polymer mobility in silica dispersions, where it was found that solvent can be immobilized by both the silica surface and by surface-adsorbed polymer layers (22).

$T_1$  experiments have been similarly used to study the adsorption of a polymeric steric stabilizer onto the surface of aluminum oxide. For example, studies of suspensions containing  $Al_2O_3$  and poly(vinylpyrrolidone-co-vinyl acetate) (PVP-co-VA) revealed that the VA carbonyl carbon exhibits decreased mobility in the presence of  $Al_2O_3$ , whereas the PVP carbonyl carbon remains unaffected (23). When combined with sedimentation data, the results suggested that the PVP segment of the copolymer provides a steric barrier to flocculation, whereas the VA segment provides an "anchor" for adsorption onto the aluminum oxide surface. Analogous  $T_1$  experiments on suspensions containing alumina and PVB revealed that the motions of the main-chain and side-chain vinyl butyral carbons are unaffected by  $Al_2O_3$ , whereas the vinyl alcohol sequences are motionally constrained, and hence preferentially adsorbed (24).

These examples, although limited in number, represent important applications of solid-state NMR relaxation experiments. Namely,  $T_1$  spin lattice relaxation experiments can be used to provide dynamic, structural, and morphological information about many types of polymer systems. This

information, in turn, can be used to develop important structure-property relationships for the purpose of advancing our fundamental understanding of macromolecules.

## 1.5 SPIN LATTICE RELAXATION IN THE ROTATING FRAME ( $T_{1\rho}$ )

§ *“It was around that time that Fernanda got the impression that the house was filling up with elves. It was as if things, especially those for everyday use, had developed a faculty for changing location on their own.”*

Spin lattice relaxation times in the rotating frame ( $T_{1\rho}$  values) are sensitive to molecular motions that occur in the kHz region. These motions are usually defined to a lesser degree than the motions that influence  $T_1$  relaxation times (11). This is because kHz regime motions are typically associated with cooperative polymer backbone rearrangements that envelop the collective motions of a large number of monomer units (3). Long-range, cooperative motions such as these are considered to be the motions that define a polymer's response to mechanical perturbations (9, 10).

During a  $^{13}\text{C}$   $T_{1\rho}$  experiment, the lower energy  $^{13}\text{C}$  populations (the nuclei aligned with the external field) are enhanced through cross polarization with the proton dipolar reservoir. This is accomplished by first spin-locking the proton nuclei so that they precess at a kHz frequency, which is independent of the external magnetic field. The  $^{13}\text{C}$  nuclei are then subjected to an appropriate field such that the Hartmann-Hahn match condition is met ( $\omega_{\text{C}}\gamma_{\text{C}} = \omega_{\text{H}}\gamma_{\text{H}}$ ). The proton field is then removed for variable time periods so that the rate of  $^{13}\text{C}$  decay in the rotating frame can be measured (25).

The mechanism of relaxation during a  $T_{1\rho}$  experiment is analogous to the spin lattice relaxation mechanism that occurs during a  $T_1$  experiment. However, the difference is that  $T_{1\rho}$  is inversely proportional to the spectral density of motion in the kHz frequency region. Also, unlike  $T_1$ , secondary spin-spin relaxation

processes sometimes veil the spin-lattice, or motional, contributions to  $T_{1\rho}$ . Spin-spin relaxations are not directly influenced by motion alone. Thus, the direct motional interpretation of  $T_{1\rho}$  data can sometimes be difficult. This difficulty is most likely to be encountered in highly crystalline or tightly coupled spin systems (26).

The spin-spin contribution to  $^{13}\text{C}$   $T_{1\rho}$  relaxation has been treated extensively by VanderHart and Garroway (27, 28). They have shown that if  $T_{1\rho}$  is dominated by spin-spin relaxation, then a plot of  $\ln(1/T_{1\rho})$  vs. the dipolar decoupling frequency will yield a straight line with a slope that scales with the correlation time of the proton dipolar reservoir. If  $T_{1\rho}$  is modulated by molecular motion in the kHz region, then  $1/T_{1\rho}$  will vary linearly with  $1/\omega^2$ .

VanderHart and Garroway performed their studies on polyethylene and polypropylene, mainly because these polymers are highly crystalline, and because they have tightly coupled spin systems. They concluded that there are at least two ways by which to overcome the spin-spin contributions to  $T_{1\rho}$ : either increase the rf decoupling frequency to greater than 80 kHz, or increase the temperature of the system.

Schaefer et al. (29) illustrated another quantitative method to determine the spin-spin contribution to  $T_{1\rho}$ . They used the ratio of  $T_{1\rho}$  to  $T_{\text{CH-ADRF}}$ , where  $T_{\text{CH-ADRF}}$  (proton-to-carbon cross polarization via adiabatic demagnetization in the rotating frame) is the cross polarization rate of the  $^{13}\text{C}$  nuclei, with the local dipolar order that is established upon turning off the proton spin lock pulse (not the direct CP with spin-locked protons as would normally be the case). The  $T_{\text{CH-ADRF}}$  value is an indicator of the amount of spin-spin contribution to the  $T_{1\rho}$  relaxation process. When the  $T_{1\rho}$  to  $T_{\text{CH-ADRF}}$  ratio approaches zero, there is no spin-spin contribution, and  $T_{1\rho}$  is strictly influenced by kHz frequency motions. When the ratio is equal to one,  $T_{1\rho}$  is influenced entirely by spin-spin relaxation processes.

Schaefer et al. have also provided several qualitative arguments, which can be used to determine the importance of spin-spin contributions to  $T_{1\rho}$ . For example, they have noted that the spin-locked cross polarization rates ( $T_{CH}$ 's) and the  $T_{1\rho}$ 's for two different carbon centers (differing only in the number of directly bonded protons) should vary according to a fixed relationship that depends on the relative contribution of spin-spin relaxation processes. If the spin-spin contribution is important, then both the  $T_{CH}$ 's and  $T_{1\rho}$ 's for the two carbons should differ by a factor that is equal to the difference in the number of protons that are directly bonded to each carbon center.

Hence, it is possible, particularly in amorphous systems, to perform  $T_{1\rho}$  experiments without experiencing complications from spin-spin contributions. Schaefer et al. have successfully performed these experiments on a variety of glassy polymers (8,17, 29,30,31). An example considered to be classic involved their correlation of the  $T_{CH}/T_{1\rho}$  ratio with the impact resistance of several glassy polymers (8). This was the first work to particularly emphasize the importance of relating near-static and kHz regime motions to mechanical behavior. Upon application of ideas originally appreciated by Farrar and Becker (9), Schaefer et al. suggested that a polymer's spectral density (as approximated by  $T_{CH}/T_{1\rho}$ ) dictates its macroscopic response to a mechanical impact. It was further suggested that a polymer should exhibit its optimum impact resistance when its spectral density distribution (i.e., its capacity for energy adsorption through molecular motion) is coincident with the frequency components that are delivered during an impact. Although this work was generally considered to be a promising start towards relating molecular motions to mechanical properties, many questions still remain about the role of cooperative motional units, particularly in multi-phase polymeric systems (13).

Like its  $T_1$  counterpart,  $T_{1\rho}$  can also provide information about motional heterogeneity in multi-component, phase-separated systems. However, unlike  $T_1$ , which is predominantly influenced by localized motional processes,  $T_{1\rho}$  is

influenced by long-range cooperative motion. Consequently, the motion in one morphological domain may be dramatically affected by motional changes in other domains, through what is described as motional cooperativity between phases. This phenomenon was observed by Christenson et al. (26) in their studies of model polyurethane systems. They found that the "hard-segment" domains are composed of motional units, which are influenced by the motion that occurs in the "soft-segment" domains. Similar results were observed by Marcinko (32) in studies of wet and dry polyurethane systems.

The differences between  $T_1$  and  $T_{1\rho}$  were further exemplified by Ritchey (5), and by Schaefer (13) in their studies of plasticized polymer systems. Namely, they found that  $T_{1\rho}$  responds to a change in plasticizer concentration, whereas  $T_1$  is generally not affected. Ritchey used  $T_{1\rho}$  experiments to show that bis-dioxane preferentially associates with the methoxy groups of PMMA. Similarly, Schaefer observed that DHA decreases the  $T_{1\rho}$  values for the main-chain carbons in poly(vinyl butyral). Neither of the research groups was able to delineate these effects with  $T_1$  measurements alone.

## 1.6 LINE BROADENING AND MOLECULAR MOTION – DEUTERIUM AND CARON-13 NMR

§ "...*We're going to rot our lives away here without receiving the benefits of science. That certainty, mulled over for several months in the small room he used as his laboratory, brought him to the conception of the plan to move Macondo to a better place.... He tried...with the charm of his fantasy, with the promise of a prodigious world where all one had to do was sprinkle some magic liquid on the ground and the plants would bear fruit whenever a man wished, and where all manner of instruments against pain were sold.... But Úrsula was insensible to his clairvoyance...*"

Generally speaking, line broadening in solid polymers occurs when the density of molecular motion is too low to sufficiently average the net dipolar, quadrupolar, and CSA interactions to zero. Thus, the degree of line broadening as a function of temperature can provide important motional information about a

polymer system. Line broadening in both deuterium and  $^{13}\text{C}$  spectroscopy can be used for this purpose.

Deuterium is a quadrupolar nucleus (spin  $I = 1$ ), and as such, it is susceptible to a strong electric quadrupole interaction that often leads to very broad "powder patterns" in the solid state (ca. 200 kHz) (30). The high strength of the quadrupole interaction also means that the line-widths in deuterium spectroscopy will be particularly sensitive to motional heterogeneity, and to changes in motional dynamics.

Jelinski et al. (31) have used deuterium spectroscopy to elucidate two distinct motional regions in copolymers of selectively deuterated poly(butylene terephthalate) (PBT) and poly(tetramethyleneoxy terephthalate) (PTMT). Specifically, the PBT hard segments are characterized by a broad line pattern that arises as a result of limited molecular motion. However, the PTMT amorphous phase undergoes more extensive motion, as was indicated by an extreme narrowing of the deuterium spectrum.

Simple  $^{13}\text{C}$  spectra at various temperatures can also yield information about motional heterogeneity. Flemming et al. (14) have noted that  $^{13}\text{C}$  line broadening occurs when the frequency components of molecular motion approach the dipolar decoupling frequency (typically 40 to 100 kHz). During observations of both polypropylene and PMMA at lower temperatures, they noted an increase in  $^{13}\text{C}$  line broadening due to a decrease in the kHz frequency components of methyl group reorientation. The line broadening was observed to reach a maximum at the temperature where the methyl group reorientation rate was coincident with the dipolar decoupling frequency. As they continued to lower the temperature, the methyl reorientation rate began to move out of phase with the proton decoupling frequency, and the  $^{13}\text{C}$  lines became narrow again.

Garroway and Ritchey (33) have used this phenomenon to study glassy-state molecular motions in solid epoxy polymers. Upon lowering the temperature, they noted that the  $^{13}\text{C}$  resonance bands for a phenylene group were split into two



distinct peaks. By further lowering the temperature, the motional "flipping" of the phenylene group was suppressed, the isotropic motional averaging of the CSA interaction was lifted, and two distinct chemical environments were observed to appear. A two-site exchange model was used to calculate the activation energy for the temperature-dependent inter-conversion process. The activation energy (15 kcal/mol) was in agreement with values that were determined separately from mechanical spectroscopy data.

Parker et al. (34) have also observed a temperature-dependent line broadening pattern for the backbone carbons of PVB, where the maximum broadening (as measured at an effective proton decoupling frequency of 57 kHz) was found to occur at a temperature of approximately 50°C above the  $T_g$  (as measured by DSC). Using Arrhenius plots, the NMR transition was confirmed to correlate with the glass transition as measured separately by means of DMA and DSC techniques.

## 1.7 CROSS POLARIZATION TECHNIQUES AND POLYMER MORPHOLOGY

§ *"...he spent entire nights in the courtyard watching the course of the stars.... He conceived a notion of space that allowed him to navigate across unknown seas, to visit uninhabited territories, and to establish relations with splendid beings without having to leave his study. ...it was possible to cross the Aegean Sea on foot by jumping from island to island all the way to the port of Salonika."*

The rate of cross polarization is inversely related to the density of molecular motion in a polymer system (8). Thus, cross polarization rates can be used to determine the extent of motional heterogeneity and phase separation in a polymer system. Inversion recovery cross polarization NMR (IRCP) and CPMAS of deuterated blends are techniques that take advantage of the relationship between the cross polarization rate and motional heterogeneity to yield information about morphology.

IRCP is analogous to the  $T_1$  inversion recovery technique, since both techniques can be used to selectively null out the spectral contribution of one component in a multi-component system. However, the IRCP technique can be used to unambiguously discriminate between rigid and mobile components, whereas the use of a standard  $T_1$  technique requires knowledge of the relative position of each  $T_1$  minimum (from a  $T_1$  vs. temperature curve) before any such distinction can be made.

Cory and Ritchey (35) have used the IRCP technique to elucidate the amorphous and crystalline components of polyethylene and poly(oxymethylene). They have pointed out that this technique does not require spectral subtraction, nor does it require the long experimental times that are required for  $T_1$  inversion recovery. However, its use may be limited to systems with components that have largely different cross polarization rates.

Using the premise that  $T_{CH}$  is affected by near static motion, Parker et al. (36) and Marcinko et al. (37) have established correlations between  $T_{CH}$  values (as measured by IRCP) and dynamic storage moduli (as measured by DMA) for a diverse set of polymers. The empirical correlation was subsequently expressed in terms of two independently derived models, where the cross polarization rate was expressed as a function of the correlation time for the fluctuation of the dipolar reservoir, and the dynamic storage modulus was expressed as a function of the correlation time for a dashpot in a Maxwell-Weichert dashpot-spring model. In turn, the resultant correlation constant ( $2.95 \times 10^{-5} \text{ sec}^2$ ) was used to estimate the viscosity of a liquid in a heterogeneous suspension (38), and to estimate the effective modulus of the organic polymer phase in a heterogeneous polymer composite (39). Thus, by measuring the cross polarization rate,  $T_{CH}$ , it is possible to estimate the “correlation time” for near static molecular motion, and in turn, to determine the rheological and mechanical contributions of organic polymers to the macroscopic properties of composite systems.

Another important technique for studying the morphology of polymer/polymer and polymer/plasticizer blends relates to the use of CPMAS experiments on mixed systems comprised of both deuterated and protonated polymers. This technique is particularly advantageous for studying blends in which the individual components can be considered amorphous.

Porter et al. (40) have used this technique to investigate the compatibility of PVC/PMMA and PS/PVME blends. Generally, in these studies, one of the polymers is deuterated, while the other is protonated. The efficiency of cross polarization during a CPMAS experiment will depend on the compatibility of the two polymers. When the deuterated polymer is incompatible with the protonated polymer, the transfer of polarization from the proton dipolar reservoir of the protonated polymer to the carbons of the deuterated polymer will be inefficient. On the other hand, an efficient transfer of polarization would indicate that the two polymers are compatible.

Cross polarization will occur if the distances between the carbons of the deuterated polymer and the protons of the protonated polymer are about 10 angstroms or less. Thus, when two polymers are partially compatible, the CPMAS technique can yield information about the amount of blending that occurs near the interfacial regions that separate the morphologically-distinct phases.

Cross polarization techniques have also been used to study the motional dynamics of low-molecular weight molecules in high-molecular weight polymer matrices. For example, NMR studies of plasticizer motions in poly(vinylbutyral)-plasticizer blends (41) have revealed that a portion of the plasticizer has the mobility of a neat liquid, whereas another portion has the relative rigidity of the surrounding polymer matrix.

In another account, cross polarization and scalar-decoupling techniques were used to study the hydrolysis reaction and the motional dynamics of phenylaminopropyltrimethoxysilane in a plasticized poly(vinyl chloride) (PVC)

polymer matrix (42). The plasticized PVC/silane blend was laminated to glass under conditions of high pressure and high temperature. Qualitatively, the adhesion strength of the polymer to glass was observed to increase when the plasticized PVC/silane blend was exposed to a high-humidity environment prior to lamination. Importantly, the hydrolysis reaction (as followed by NMR) was observed to depend on both the atmospheric conditioning of the polymer matrix, and on its exposure to heat during thermal processing. With the help of NMR, it was determined that the hydrolysis reaction did not occur until after the humidity-exposed sheet was subjected to the high temperature lamination process.

In addition, a portion of the silane was observed to exhibit liquid-like mobility, while another portion was observed to share the solid-like rigidity of the surrounding polymer matrix. Interestingly, the fraction of silane having solid-like rigidity was observed to increase with increasing hydrolysis (paralleling the increase in adhesion strength). Thus, as this example shows, NMR techniques can be used to establish important links between 1) molecular-level variables (i.e., hydrolysis and motional dynamics); 2) macroscopic-level variables (i.e., thermal history and environmental process history); and 3) macroscopic-level properties (i.e., adhesion).

## 1.8 CONCLUSIONS

§ *“Things have a life of their own,” the gypsy proclaimed with a harsh accent. ‘It’s simply a matter of waking up their souls.’”*

Solid state NMR experiments are capable of providing information about the motional heterogeneity in polymer systems. This type of information can in turn be used to elucidate information about morphology in semi-crystalline and bi-amorphous systems.

All of the techniques mentioned in this paper are capable of providing different types of motional information. The value of each technique can be summarized as follows:

1. Inversion Recovery  $T_1$  - Sensitive to localized MHz motions; provides information about morphology and motional differences between phases in multi-phased systems (only sensitive to differences at the MHz level);
2. Rotating Frame  $T_{1\rho}$  - Sensitive to localized kHz motions; capable of distinguishing between morphologically-distinct phases in which the motional characters differ in the kHz region; may provide information about motional cooperativity between phases;
3. Line Broadening - Deuterium spectra can provide information about phase separation and morphology;  $^{13}\text{C}$  broadening as a function of temperature can provide information about specific molecular motional processes;
4. Cross Polarization Techniques – IRCP can distinguish between "rigid" and "mobile" components;  $T_{\text{CH}}$  is sensitive to low-frequency motions and may provide information about long-range cooperativity between motional units; and the efficiency of CP in deuterated/protonated polymer blends can provide information about compatibility at the microscopic level.

Each technique has limited utility by itself. However, when used collectively, these techniques can provide a well-rounded picture of the dynamics and morphology of a polymer system. Perhaps the biggest shortcoming at this point would be the inability of these techniques to provide detailed information about the motional cooperativity between localized motional regions. This topic will require extensive future research, and it may be the key to ultimately understanding the relationships among morphology, molecular motions, and mechanical properties.

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