Decomposition of Overlapped Solid-State ^{13}C NMR Resonances Belonging to Different Stereosequences in an Atactic Polymer

Hajime Tanaka,[†] **M. A. Gomez,**[‡] **and A. E. Tonelli***

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received January 6, 1988; Revised Manuscript Received April 14, 1988*

ABSTRACT: We clearly show for the first time that the broad resonance of the α-methyl carbon observed in the CP MAS/DD ^{13}C NMR spectrum of atactic poly(methyl methacrylate) (PMMA) can be decomposed to three peaks corresponding to different tacticities (rr, rm (mr), and mm) by taking advantage of the differences in the rotational motions of the α-methyl carbons in these stereoenvironments. We find the T_1's of the α-methyl carbons in atactic PMMA strongly depend on tacticity. The dependence of rotational motions on local conformation is discussed, and the cross-polarization dynamics are also shown to reflect the local conformation. This method, which depends on tacticity-related motional differences, can be applied to other atactic polymers in order to resolve overlapped solid-state peaks into their individual stereoisomeric contributions.

Generally, high-resolution ^{13}C nuclear magnetic resonance (NMR) gives information concerning both the conformational and motional states of macromolecules. Usually molecular motion is closely related to the conformations of polymers. This correlation between molecular motion and local conformation provides us with a new method for resolving overlapping peaks of an atactic polymer with different tacticities in the solid state. In the solid state, the line width is generally broad enough to smear out information on the chemical shift difference of carbons belonging to different stereosequences, even if high-power dipolar decoupling and magic angle spinning are employed. Correlation between the tacticity and the motional state of an atactic polymer in the solid state has not been studied. It should give important information concerning the effects of local environment on local motion.

There are several possible techniques for resolving overlapping peaks by the use of differences in molecular motion. In solid-state NMR, the motional state is reflected by the spin–lattice relaxation time T_1 of ^{13}C, that in the rotating frame $T_{1\rho}$, T_1 and $T_{1\rho}$ of ^{1}H, the spin–spin relaxation time T_2 of ^{1}H, and that of ^{13}C. Among these relaxation times, T_1 and $T_{1\rho}$ of ^{1}H yield no information on local conformation because of spin diffusion. On the other hand, T_1 of ^{13}C is free from spin diffusion effects because ^{13}C is a rare spin. T_2, or the second moment, can also provide local information because the dipolar interactions have very short-range character. Here we consider the use of differences in $T_1(^{13}\mathrm{C})$ and in the cross-polarization dynamics caused by local conformational differences.

Differences in molecular motion due to conformational differences or different molecular environments can produce different $T_1(^{13}\mathrm{C})$'s for each carbon with a unique chemical shift. If a resonance is composed of n different chemical shifts, the envelope shape $S(f)$ during the T_1 experiment is described by the following equation

$$S(f) = \sum_i S_i(f) \exp(-t/T_1(i)) \qquad (1)$$

where S_i is the line shape of the i-th chemical shift at $t = 0$ and $T_1(i)$ is the T_1 of the i-th carbon chemical shift.

If there is a large difference in $T_1(^{13}\mathrm{C})$'s between different chemical shifts, the envelope shape should change as a function of the waiting time, τ. We can choose temperature appropriately to create the maximum difference in $T_1(^{13}\mathrm{C})$'s, which gives us the maximum contrast.

We may apply this technique to the overlapped peaks caused by the different tacticities in atactic polymers. Among the stereoisomers there are no differences in the number of directly bonded protons nor in the distances between carbons and directly bonded protons. Therefore, differences in $T_1(^{13}\mathrm{C})$'s come only from the differences in local motion and in distances between nonbonded protons. Namely, the differences in $T_1(^{13}\mathrm{C})$'s directly reflect local environments.

The same kind of experiment is possible for the cross-polarization process. If there is a T_2 difference between the protons which interact with carbons of different chemical shift during the cross polarization, the envelope shape depends on the cross-polarization time τ_{CH} as in the following equation, if we neglect the $T_{1\rho}$ process of the protons:

$$S(f) = \sum_i S_i(f)(1 - \exp(-t/\tau_{\mathrm{CH}}(i))) \qquad (2)$$

The cross-polarization time is proportional to the product of the second moment of the ^{1}H–^{13}C coupling Hamiltonian and the spectral distribution function for the cross-polarization process. If the Hartmann–Hahn condition is satisfied

$$\tau_{\mathrm{CH}} = C_{\mathrm{CH}} \langle \Delta\omega^2 \rangle_{\mathrm{CH}} \langle \Delta\omega^2 \rangle_{\mathrm{HH}}^{-1/2} \qquad (3)$$

where C_{CH} is a constant and $\langle \Delta\omega^2 \rangle$ the second moment. τ_{CH} depends on both the average distance between nuclei and their motional states and gives information different from $T_1(^{13}\mathrm{C})$.

The sample studied in this paper was atactic poly(methyl methacrylate) (PMMA) (Aldrich Chemical, $M_w \sim 93\,300$ and $M_n \sim 46\,400$). From the ^{13}C NMR spectrum recorded in solution (35 wt % PMMA in trichlorobenzene/deuteriated benzene (9/1)), we determined the fractions of the three triad stereosequences as 5% mm, 43% mr (rm), and 52% rr. Solid-state ^{13}C NMR spectra were recorded at ambient temperature on a Varian XL-200 spectrometer at a static field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 kHz was achieved with a Doty Scientific probe, which utilizes a double air bearing design. The PMMA sample was spun in aluminum oxide rotors with Kel-F [poly(chlorotrifluoroethylene)] end caps. A 45-kHz rf field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The pulse width of $\pi/2$ was 5.0 μs. The optimum cross polarization (CP) time was found to be 2 ms. The $T_1(^{13}\mathrm{C})$ experiment was performed under the CP condition by application of the pulse sequence developed by Torchia.[1] This pulse sequence is a combination of cross polarization and inversion recovery. The time during which the spin interacts with

---

[†] Permanent address: Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

[‡] Permanent address: Instituto de Plasticos y Caucho, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain.

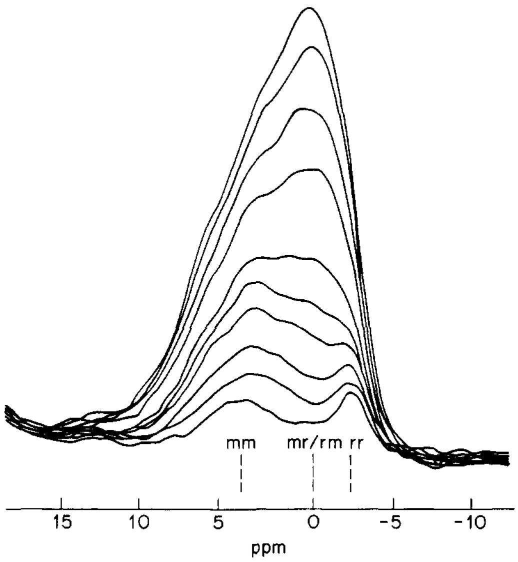

Figure 1. Change of shpae of α-methyl resonance as a function of τ in the CP-T_1 experiment. Spectra correspond to τ = 5, 10, 20, 30, 60, 80, 100, 140, 200, and 300 ms, respectively, from the top to the bottom.

the lattice is expressed by τ.

We focus our attention on the broad α-methyl resonance of PMMA. This resonance is composed of at least three peaks corresponding to the different triad stereosequences, rr, rm (mr), and mm. Figure 1 shows the decay process of the signal from the α-methyl carbon for various τ values measured by the CP-T_1 pulse sequence under the cross polarization time of 2 ms. It is clear that there are three peaks with different chemical shifts and $T_1(^{13}C)$'s. The relative chemical shift differences for the three peaks are +4.3, 0, and -2.4 ppm. The peaks are assigned to mm (isotactic), rm and mr (heterotactic), and rr (syndiotactic) triads, respectively, from downfield to upfield by comparison with the solution spectrum. In solution, the chemical shifts for mm, rm (mr), and rr are 21-22 (2-3), 19 (0), and 17.2 (-1.8) ppm from TMS (from the central peak), respectively.[2,3] The chemical shift differences are larger in the solid state compared to solution. This may be a result of the absence of conformational averaging in solid PMMA below its glass transition T_g. Our recent NMR measurements at high temperature show that the solid-state chemical shift differences approach the differences in solution especially above T_g. The line width of mm is broader than that of rr. This seems to be because of a sensitivity to tacticity higher than triads or to the efficiency of dipolar decoupling.

Due to the breadth of the solid-state resonances (see Figure 1), we assume that the intensity at +4.3 ppm is a combination of mm and mr (rm) resonances. We extract two T_1 values $\{T_1(\text{mm}), T_1[\text{mr(rm)}]\}$ with a double exponential (see eq 1). Similarly, the intensity at -2.4 ppm is assumed to be a sum of rr and mr (rm) resonances, and once again a double exponential is used to extract two T_1's$\{T_1(\text{rr}), T_1[\text{mr(rm)}]\}$. Finally, the intensity at 0.0 ppm is treated as originating exclusively from the mr (rm) resonance, and a single exponential leads to $T_1[\text{mr(rm)}]$. It should be mentioned that the same $T_1[\text{mr(rm)}]$ is obtained from all three (+4.3, 0.0, and -2.4 ppm) intensity versus τ measurements. The $T_1(^{13}C)$ of mr (rm) is found to be shortest, that of mm intermediate, and that of rr longest.

These results clearly demonstrate the possibility of decomposing a broad solid-state resonance composed of several chemical shifts by use of their motional differences.

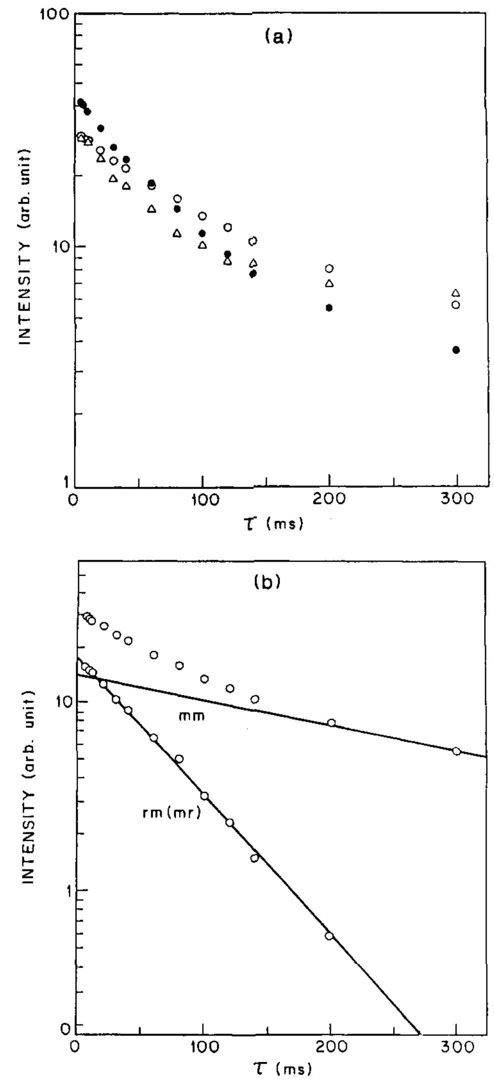

Figure 2. (a) Change of intensity at three different chemical shift positions as a function of τ: (○) +4.3 ppm (mm); (●) 0 ppm (rm, mr); (△) -2.4 ppm (rr). (b) Example decomposition of signal intensity at the relative chemical shift of +4.3 ppm (mm) into two processes.

Figure 2a shows the intensity of the three chemical shifts corresponding to mm, rm (mr), and rr plotted against τ. From decomposition of the T_1 decay process (see eq 1 and Figure 2b), we obtain T_1 at 23 °C for mm, rm (mr), and rr as 400, 50, and 800 ms, respectively. Preliminary measurements at higher temperatures indicate that all three resonances are on the show-motion sides of their T_1 minima.

Rotation of the α-methyl groups in PMMA has been studied by NMR and neutron scattering both in the solid and in solution by several groups.[4-6] The α-methyl rotation in stereoregular syndiotactic and isotactic PMMA was studied. To our knowledge, however, there has been no study of the effect of tacticity on α-methyl rotation in atactic PMMA. Heretofore, the α-methyl peak has been dealt with as a single broad resonance.

According to Edzes and Veeman,[4] the $T_1(^{13}C)$ of the α-methyl carbon of solid PMMA is 50, 100, and 53 ms for atactic, isotactic, and syndiotactic PMMA, respectively. The resonance frequency of their measurements, 45.27 MHz, is comparable with ours. More recent results[5] of ^{13}C NMR also suggest that the T_1 of syndiotactic PMMA is shorter than that of a more isotactic sample. Also room temperature is very close to the T_1 minimum temperature, and the molecular motions have frequencies similar to the

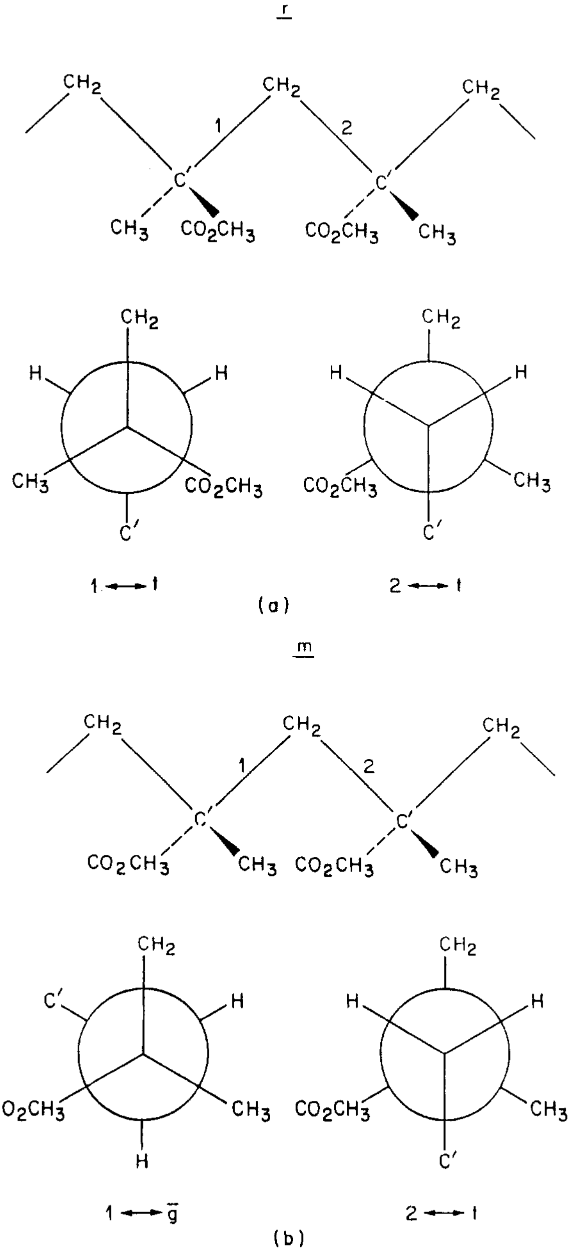

Figure 3. Schematic drawing of r and m PMMA diads. (a) Newman projections along bonds 1 and 2 in the tt conformation. (b) Newman projections along bonds 1 and 2 in the g̅t conformation. Note in (b) that when bond 1 is g̅ only the vicinal methylene protons are able to hinder the α-methyl rotation.

resonance frequency at room temperature.

The T_1's of mm and rr α-methyl carbons in atactic PMMA are much longer than those found in isotactic and syndiotactic PMMA. This difference may be because of (1) different conformations in atactic, isotactic, and syndiotactic PMMA or (2) problems associated with the measurement of T_1 in stereoregular polymers. Stereoregular polymers, especially syndiotactic PMMA, contain significant amounts of heterotactic component, which might cause the shorter T_1's reported.

Figure 3 shows schematic drawings for two different conformations of PMMA. According to our results, even in atactic PMMA, there are large differences in the rotational motions of the α-methyl groups. This suggests that methyl rotation is mainly affected by very local conformation, probably nearest-neighbor groups via intramolecular interactions with little intermolecular contributions. Methyl rotation is determined by steric hindrance from nearest-neighbor groups.[6,7] The difference between T_1's of local rr and mm conformations in atactic PMMA and those of syndiotactic and isotactic PMMA should give information concerning the intermolecular effects of interference on α-methyl rotation.

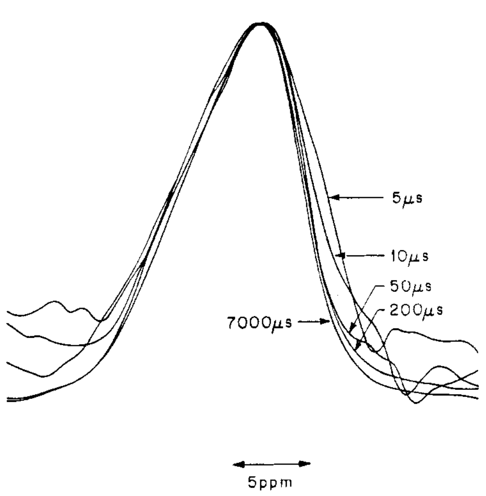

Figure 4. Change of shape of the α-methyl resonance as a function of the contact time. The spectra correspond to τ_{CH} = 5, 10, 50, 200, and 7000 μs from the widest to the narrowest, respectively.

Both neutron scattering and NMR relaxation studies[6] yield 3-fold α-methyl rotation barriers of 32 and 23 kJ/mol respectively for solid syndiotactic and isotactic PMMA. The relative size of these barriers was rationalized by estimation[6] of the energy required for α-methyl rotation in syndiotactic and isotactic PMMA when placed in their prefered conformations. Vacatello and Flory[8] find the all-trans (t), nearly planar, zigzag conformation to be most favored for syndiotactic PMMA, while the g̅t backbone conformation is most likely in isotactic PMMA. When the backbone is t, the α-methyl group is close to the methylene proton and the quaternary carbon three bonds removed. In the g̅ conformation only the two vicinal methylene protons are close to the α-methyl groups. Since the g̅ conformation is more likely in isotactic PMMA and would appear to permit more facile α-methyl group rotation than the t conformation, it seems possible to understand the lower barrier to α-methyl rotation found in isotactic PMMA. The shorter T_1 observed for the mm stereosequence in an atactic PMMA sample compared to the rr stereosequence also seems reasonable in light of this discussion.

To explain the anomalously large differences in T_1 between stereosequences, we should also think about another possibility: The large differences in the T_1 values between stereosequences might be a result of the existence of another kind of motion which affects the motion of the α-methyl carbon. The most probable candidate for such a motion is a backbone motion which should be activated around T_g. In this regard, we are now studying the temperature dependence of T_1 for the different stereosequences in atactic PMMA.

The discussion relating the T_1's of the α-methyl carbons in PMMA directly to the barrier hindering their rotation presupposes that the three directly bonded α-methyl protons are exclusively responsible for relaxing the α-methyl carbon. Because the dipole–dipole interaction depends on r_{CH}^{-6}, the contributions to $T_1(^{13}C)$ from neighboring nonbonded protons ($r_{CH} > 2$ Å) are expected[2] to be insignificant compared to those from the directly bonded α-methyl protons ($r_{CH} = 1.09$ Å).

Finally we consider the effect of tacticity on cross-polarization dynamics of the α-methyl carbon of PMMA.

Figure 4 shows the change of the peak shape as a function of cross-polarization time. All the spectra were normalized for the comparison of shape. Compared to the CP–T_1 experiment, the shape change is not so obvious. This is reasonable because there are no large differences in T_2 in the glassy state. However, the situation might be different near the glass transition point. There is a slight narrowing of line width with increasing contact time. From ^{13}C NMR measurements in solution, the fraction of each triad stereosequence in our atactic PMMA sample has been estimated as 5% mm, 43% mr (rm), and 52% rr. The α-methyl resonance in the solid-state CP/MAS spectra appears to contain much more than 5% mm component[4] because of efficient cross-polarization dynamics. On the other hand, the rr component must be inefficiently cross polarized, judging from the reduced intensity observed for this triad stereosequence. For a more quantitative discussion, we need to be able to decompose the broad α-methyl resonance into individual stereosequence components. Generally, if there is some difference in τ_{CH}, there should be a change of shape until $\max(\tau_{CH}(i))$. For τ_{CH} more than $\max(\tau_{CH}(i))$, there is no shape change because the $T_{1\rho}$ for these individual peaks should be similar due to spin diffusion in the homogeneous homopolymer. Actually, we observe no shape change for contact times of more than 2 ms.

We have demonstrated the possibility of decomposing the broad α-methyl resonance observed in the CPMAS spectrum of atactic PMMA into its individual stereoisomeric peaks. This separation is made possible by the different rates of rotation, as reflected by different T_1's, for the α-methyl groups in each stereosequence. Comparison of the α-methyl T_1's measured here for the mm, mr (rm), and rr stereosequences in atactic PMMA to those observed in stereoregular isotactic and syndiotactic PMMA may indicate a sensitivity to interchain packing which is different between the crystalline stereoregular PMMA's and the amorphous atactic sample.

We are now studying the temperature dependence of T_1 for each stereosequence to make clear the origin of the large difference in T_1 values between stereosequences and the effect of motion on the averaged values of chemical shift anisotropy tensors. The detailed results will be published elsewhere.

Registry No. PMMA, 9011-14-7.

References and Notes

(1) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(2) Lyerla, J. R., Jr.; Horikawa, T. T.; Johnson, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2463.
(3) Heatley, E.; Begum, A. *Polymer* **1976**, *17*, 399.
(4) Edzes, H. T.; Veeman, W. S. *Polym. Bull. (Berlin)* **1981**, *5*, 255.
(5) Gabrys, B.; Hori, F.; Kitamaru, R. *Macromolecules* **1987**, *20*, 175.
(6) Allen, G.; Wright, C. J.; Higgins, J. S. *Polymer* **1974**, *15*, 319.
(7) Gabrys, B.; Higgins, J. S.; Ma, K. T.; Roots, J. E. *Macromolecules* **1987**, *17*, 560.
(8) Vacatello, M.; Flory, P. J. *Macromolecules* **1986**, *19*, 405.

Spectroscopic Studies of Diluent Motion in Glassy Plasticized Blends

Roger P. Kambour, John M. Kelly, and Barbara J. McKinley

Polymer Physics and Engineering, General Electric Corporate Research and Development Center, Schenectady, New York 12301

Bonnie J. Cauley, Paul T. Inglefield,* and Alan Anthony Jones

Jeppson Laboratory, Department of Chemistry, Clark University,
Worcester, Massachusetts 01610.

Received January 25, 1988;
Revised Manuscript Received April 18, 1988

ABSTRACT: No subglass transition mechanical loss peaks are observed in 50–50 blends of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene. However, if trioctyl phosphate is added to the blend the modulus lowers and a broad low-temperature loss peak appears. Nonspinning phosphorous line shapes were observed to determine if the diluent itself was moving in the glassy matrix, which is clearly the case. At low temperatures a typical axially symmetric line shape is observed which evolves to a narrow line just below the glass transition of the three-component system. The pattern of the collapse appears to take the form of a shift in population from nearly immobile diluent to fairly mobile diluent. This pattern of collapse can be associated with a broad distribution of correlation times. The geometric character of the motion of the mobile diluent is apparently isotropic rotation.

The mechanical properties of bulk amorphous polymers depend on the local chain motions present and in turn the local motions reflect the chemical structure of the repeat unit of the polymer chain. The motions are also influenced strongly by intermolecular interactions between chains so that in the glassy state the apparent activation energy of a given motion may be much higher than that expected for the same motion in an isolated polymer chain.[1] Two general strategies can be followed to control properties of amorphous polymers without changing the morphology. First, the local motions present can be changed by modifications of the chemical structure of the repeat unit; and second, intermolecular interactions can be modified by the addition of a second type of molecule to the bulk polymer. In the latter case, the second component could be either a small molecule diluent or another polymer. The addition of a second type of polymer not only modifies the intermolecular interactions but also introduces a new repeat unit structure which may have its own set of local motions distinct from the host polymer.

A recent survey[2] of the mechanical properties of a set of plasticized blends has revealed a strong dependence of