What Is the Source of the Microstructural Dependence of Resonance Frequencies Observed in the Solution NMR of Polymers Whose Local Structures and Conformations Appear To Be Independent of Their Longer Range Microstructures?

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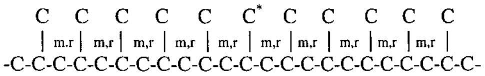
Received September 10, 2001

Introduction

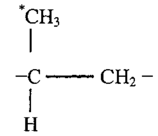
It is widely accepted that the resonance frequencies observed for chemically equivalent carbon nuclei in the high resolution, solution ^{13}C NMR spectra of polymers are sensitive to their microstructures. For example, the methyl carbons in atactic polypropylene (a-PP) samples show numerous resonances spread over more that 2.0 ppm, reflecting the various stereochemical environments present in these stereoirregular polymers. The sensitivity to stereosequence of the resonance frequencies of the methyl carbon nuclei in atactic PPs, in fact, extends to the undecad level. Below we have drawn a schematic representation of a PP undecad, and have indicated with *m*, *r* (*meso*, racemic) the relative stereochemistry of its 10 constituent diads, which leads to a staggering 528 unique undecads in all.



This means that the chemical shift or resonance frequency of the central methyl carbon in a PP undecad, C*, can be effected by the stereochemistry (*m* or *r*) of even the terminal diads, so the methyl carbon resonance frequencies in the *mmmmmmmrmr* and *mmmmmmmrmm* undecads, for example, are distinct.[1]

In Figure 1, a PP heptad is drawn to illustrate the γ-gauche shielding effect on carbon nuclei.[2] When two carbons separated by three intervening bonds, i.e., that are γ to each other, are in a gauche (g) arrangement, both are observed to be shielded by ~ -5 ppm compared to their trans (t) conformation. Thus, in the left drawing of Figure 1a, which presents the Newman projection along the backbone in the trans conformation, the methine carbon(C_α) and the methy carbon $^*CH_3$ are gauche to each other, while the methine carbon and the methylene carbon (C_β) are in a trans arrangement. As a consequence, in this backbone trans conformation both the methine and methyl carbons will experience shielding from the γ-gauche effect, while the methylene carbon will not. In the g^+ backbone conformation illustrated in the middle panel of the figure, we expect both the methine and methylene carbons to experience γ-gauche shielding, but not the methyl carbon. In the right panel in Figure 1 we can see that in the sterically crowded, highly unlikely g^- backbone conformation the methine carbon is shielded by both the methylene and methyl carbons, while each of these are shielded only by the methine carbon.

In Table 1, the probabilities of finding a central backbone bond of a-PP in the trans conformation, as calculated[2] for all pentad stereosequences with the Suter−Flory[3] RIS model for PP, are presented. Clearly the conformation of this backbone bond is sensitive to the stereochemistry of each of the constituent diads. This means that the trans−gauche populations of the backbone bonds in a-PP are stereosequence dependent, and through the γ-gauche shielding effect, the resonance frequencies must also be sensitive to long-range differences in stereosequence. Busico and Cipullo,[1] using high-field ^{13}C NMR (150 MHz for ^{13}C), have in fact detected a 0.03 ppm difference in the methyl resonance frequencies for the *mmmmmmmrmr* and *mmmmmmmrmm* a-PP undecad resonances. When the probabilities for finding the



$$-\overset{{}^*CH_3}{\underset{H}{C}}-CH_2-$$

bond belonging to the central repeat unit in the *mmmmmmmrmm* and *mmmmmmmrmr* PP undecads in the trans conformation are calculated, we find them to differ by ~0.08 at 100 °C. Clearly, both the observed resonance frequencies and local conformations of PP exhibit an exceedingly long range dependence on stereosequence.

Having demonstrated that local polymer conformations and the consequent resonant frequencies of their carbon nuclei can potentially depend on very long-range stereosequences, let us consider polymers whose repeat unit conformations are generally considered independent. Two such polymers are the stereoirregular poly(lactic acids) (PLA) and the copolymers of ethylene and butylene terephthalate (PET/PBT), which are presented schematically in Figures 2 and 3, respectively. The PLA drawing in Figure 2 illustrates a single repeat unit *i* and portions of its immediately adjacent repeat units *i* − 1 and *i* + 1, where each is of the L configuration, so this partial PLA triad is isotactic (LLL or *mm*). In Figure 3, PET/PBT terephthaloyl fragments (TP) with, two ethylene glycol (EG), two 1,4-butane diol (BD), and an EG and a BD residue attached are drawn as EG-TP-EG, BD-TP-BD, and EG-TP-BD, respectively.

It is generally assumed, because of the planar, trans character of the connecting ester bonds, that the conformations of PLA repeat units are independent of each other.[4,5] On this basis, we would anticipate that the probability of conformations φ_i and ψ_i of the central repeat unit in the PLA fragment shown in Figure 2 would not depend on the conformations ψ_{i-1} and/or φ_{i+1} of its adjacent repeat units. This should be manifested experimentally by ^{1}H and ^{13}C NMR spectra that are insensitive to PLA stereosequences if the resonances of the ^{13}C nuclei in PLA are primarily sensitive to their local conformations. However, this is not the case, because the chemical shifts or resonance frequencies of both ^{1}H and ^{13}C nuclei evidence clearly observable dependencies on PLA stereoregularity.[6,7] For example, the methine carbons show multiple resonances spread over an ~0.4 ppm range for stereoirregular PLA.

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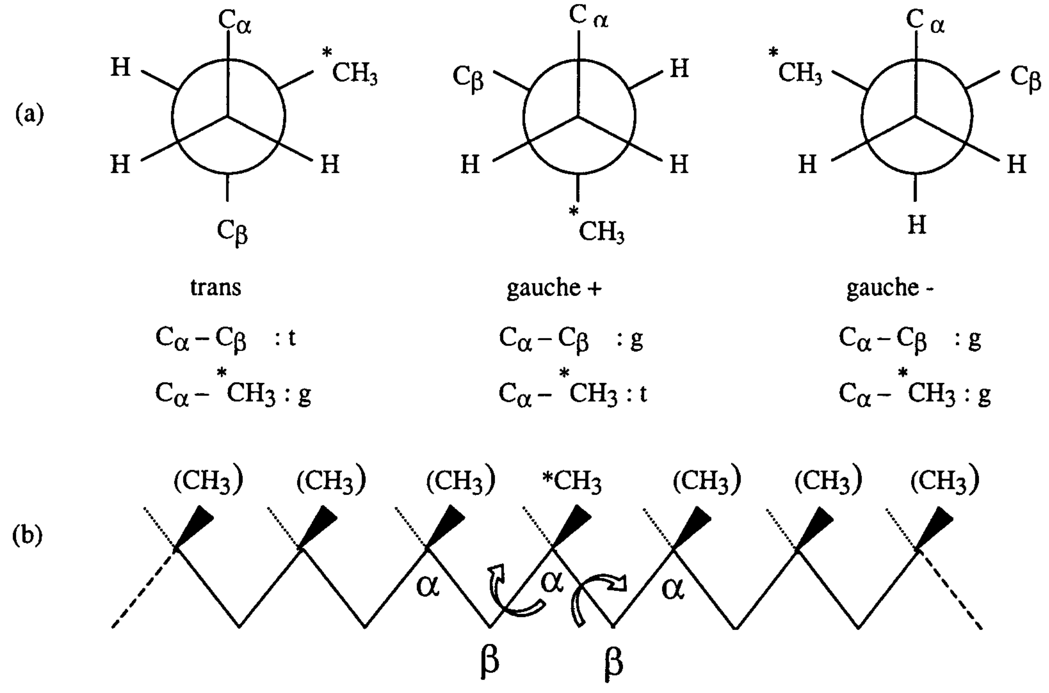
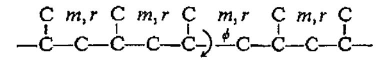


Figure 1. (a) Conformations of a four-carbon fragment of a polypropylene chain. (b) heptad of polypropylene chain, where the observed methyl is marked by an asterisk.

Table 1. Probability of Finding Bond φ in the trans Conformation Calculated for PP Pentad Stereosequences



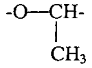
pentad stereosequence	$P(\phi = t)$
mrmr	0.440
rrnr	0.472
mmmm	0.523
rmmr	0.539
rmmm	0.582
rrrr	0.635
mrrm	0.685
rrrm	0.712
mmrr	0.742
rmrm	0.763
mmrm	0.792

Calculations

Conformational energies $E(\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1})$ were calculated for the PLA partial triad fragment of Figure 2 using the potential energy functions and geometries of Brant et al.[5] Though only the LLL triad is illustrated, the energy calculations were also performed on the LLD, DLL, and DLD stereosequence triads of PLA. The planar, zigzag representation of PLA presented in Figure 2 corresponds to all φ's and all ψ's $= 0°$. φ_i and ψ_i were averaged over all conformations $(\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1})$, where each rotation angle was stepped in 10° increments and each conformation exponentially weighted by its energy $E(\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1})$. [Though not presented here, the conformational energy map $E(\varphi_i,\psi_i)$ obtained for the PLA fragment in Figure 2 by averaging $E(\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1})$ over all ψ_{i-1} and φ_{i+1} is nearly identical to that obtained by Brant et al.[5] who considered only the interactions between atoms and groups whose distances of separation depend only on φ_i or ψ_i or both.]

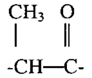
Results and Discussion

In Table 2 the average conformations $\langle\varphi_i\rangle$ and $\langle\psi_i\rangle$ for the central PLA residue i are presented. Notice that $\langle\varphi_i\rangle$ is nearly the same for the LLL, LLD, DLL, and DLD triads, so the conformation about the



$$\text{-O—}\underset{\substack{|\\ CH_3}}{CH}\text{-}$$

lactide bond does appear to be independent of the conformations of neighboring lactide repeat units. On the other hand, rotation about the



$$\text{-}\overset{\substack{CH_3\\ |}}{CH}\text{—}\overset{\substack{O\\ \|}}{C}\text{-}$$

bond or $\langle\psi_i\rangle$ changes by ~ 8° when the $i + 1$ lactide unit is changed from L to D, but is independent of the stereochemistry of the $i - 1$ lactide unit. For purposes of comparison, $\langle\varphi_i\rangle = 76.0°$ and $\langle\psi_i\rangle = 212.3°$ when averaged over only $E(\varphi_i,\psi_i)$ as calculated[5] for the independent LA residue, which corresponds to the PLA fragment in Figure 2 exclusive of the H, CH_3, C, and O atoms and groups attached to C_{i-1} and C_{i+1}.

If this small stereosequence-dependent conformational change in $\langle\psi_i\rangle$ were responsible for the stereosequence-dependent ^{13}C and ^1H resonance frequencies observed in the solution NMR spectra of stereoirregular PLAs, then we would expect only a sensitivity to LD vs LL and DL vs DD or *m* vs *r* diads. However, the number of methine carbon resonances observed,[6,7] for example, greatly exceeds this expectation. As a consequence, it appears unlikely that the dependence of lactide unit conformation on PLA stereochemistry is the source of the stereosequence-dependent ^1H and ^{13}C NMR spectra of stereoirregular PLAs.

In the case of PET/PBT copolymers, four resonances are typically observed[8,9] for both the quaternary aromatic and carbonyl carbons in their ^{13}C NMR solution spectra, which are spread over ~0.8 and ~0.5 ppm ranges, respectively. These have logically been assigned to the quaternary aromatic and carbonyl carbons adja-

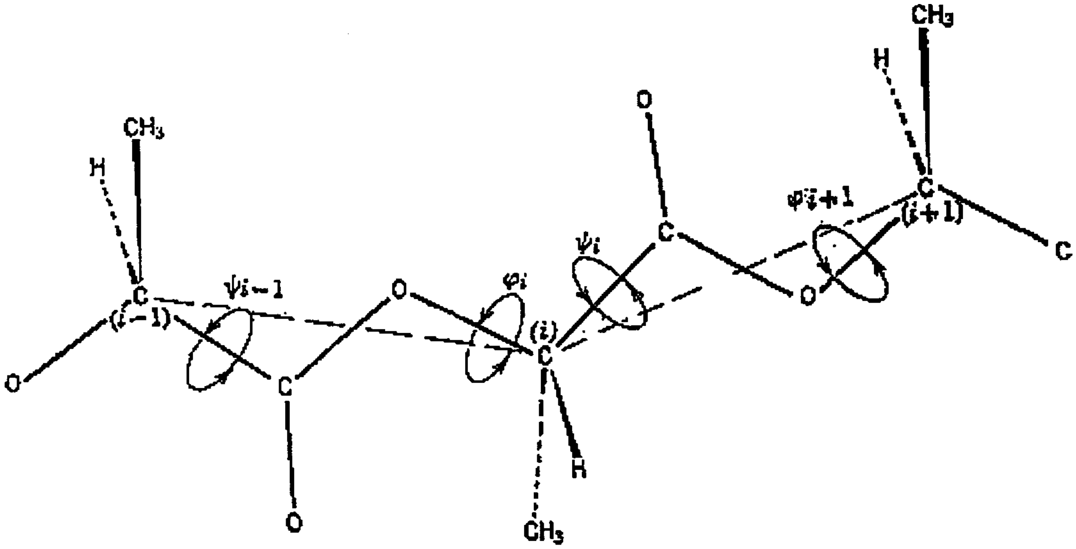
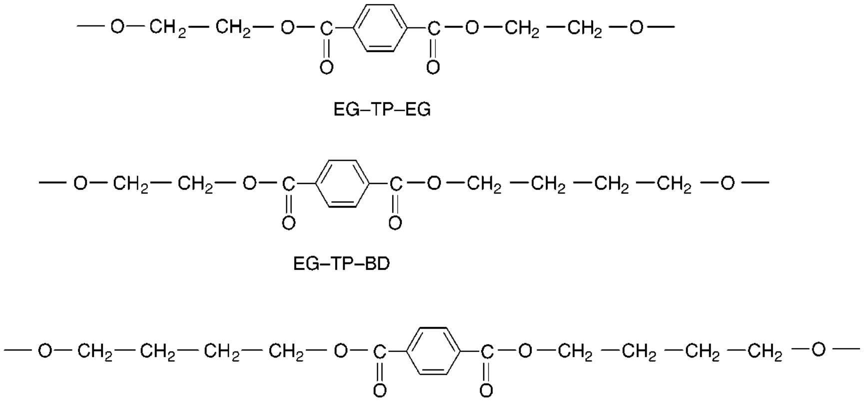


Figure 2. Partial PLA triad drawn with the LLL stereosequence, where backbone rotations in the $i-1$, i, and $i+1$ residues are indicated as $\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1}$, which have all been set to 0°.



EG–TP–EG

EG–TP–BD

BD–TP–BD

Figure 3. Schematic representations of the comonomer sequences in PET/PBT copolymers.

Table 2. Summary of Poly(lactic acid) Energy Calculations

residue $i-1$	residue i	residue $i+1$	$\langle\varphi_i\rangle$,[a] deg	$\langle\psi_i\rangle$,[a] deg
L	L	L	76.1	203.8
L	L	D	75.8	211.7
D	L	L	75.4	203.5
D	L	D	75.8	211.7

[a] Averaged over all $E(\psi_{i-1},\varphi_i,\psi_i,\varphi_{i+1})$ in 10° increments for each rotation angle.

cent to EG or BD fragments (see Figure 3), with nonequivalent chemical shifts for those TP carbons adjacent to EG(BD) in EG-TP-EG and EG-TP-BD(BD-TP-BD and EG-T-BD). So the question suggested by these observations is “Why are the resonance frequencies of quaternary aromatic and carbonyl carbons adjacent to either EG or BD diol fragments sensitive to whether EG or BD diol fragments are attached para across the phenyl ring on the opposite side of the same TP unit?”

It is difficult to believe that the conformations of EG and BD fragments are sensitive to PET/PBT comonomer sequences EG-TP-EG, EG-TP-BD, and BD-TP-BD. In X-TP-Y, where X, Y = EG or BD, the diol fragments attached to the same TP residue are separated by the full length of the TP unit, consisting of the phenyl ring and its para-attached trans ester bonds, almost certainly resulting in conformations for X, Y that are independent of each other.[4,10,11] The only remaining likely source of comonomer sequence dependent resonance frequencies for the TP carbons is the potential influence upon the delocalization of π-electrons across the TP residue produced by the attachment of two, or one of each, EG or BD. Because comonomer sequence dependent EG or BD conformations are not likely contributing to the dispersion observed for the TP carbon chemical shifts, we suggest that the most sophisticated of quantum mechanical calculational schemes should be brought to bear on the EG-TP-EG, BD-TP-BD, and EG-TP-BD frag-ments of the PET/ PBT copolymers in an attempt to understand their comonomer sequence dependent NMR resonance frequencies.

Summary and Conclusions

The ^{1}H and ^{13}C NMR solution spectra of PLA homo- and PET/PBT copolymers evidence sensitivities to microstructure (stereosequence of PLAs and comonomer sequence of PET/PBTs), which cannot be associated with the usual microstructural dependence of their local conformations, and are therefore not expected. Though not large, the ~0.4−0.8 ppm dispersions observed in the chemical shifts for the ^{13}C nuclei in PLAs and PET/PBTs having different stereo- or comonomer sequences, respectively, are not the consequence of the microstructural sensitivity of their local conformations in solution, but are nevertheless useful for their microstructural characterization. Determination of the source(s) of the microstructural sensitivity of their solution NMR spectra remains incomplete at present, but would represent a useful addition to our understanding and would enhance the capability of NMR spectroscopy to characterize both the microstructures and conformations of polymers.

Acknowledgment. We are grateful to the Department of Commerce (National Textile Center), the Army (ARO), and NCState University for supporting this work.

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MA011616R