

# Solid-state $^{13}\text{C}$ nuclear magnetic resonance investigation of poly(oxetanes): Effect of chain conformation

E. Pérez and D. L. VanderHart

National Bureau of Standards, Polymers Division, Gaithersburg, MD 20899, USA

(Received 27 June 1986)

Carbon-13 nuclear magnetic resonance (n.m.r.) in the solid state has been applied to the study of poly(oxetane) and poly(3,3-dimethyloxetane). Two different crystalline modifications, with  $T_2G_2$  and  $T_3G$  conformations, have been prepared for each of the polymers. The corresponding  $^{13}\text{C}$  chemical shifts for each sample, both amorphous and crystalline, have been determined. Single resonances for the methylene carbons  $\alpha$  to the oxygens are observed for the crystal forms having  $T_2G_2$  conformation. Two resonances are observed for these carbons in each of the crystals having  $T_3G$  conformation. The equivalence of these carbons in the  $T_2G_2$  conformation and their inequivalence, within the same monomer unit, in the  $T_3G$  conformation is a property of the isolated chain. It is argued that the observed n.m.r. inequivalence in the  $T_3G$  crystalline forms has the same origin.

(Keywords:  $^{13}\text{C}$  n.m.r.; solid state; poly(oxetanes); conformation; chemical shift)

## INTRODUCTION

High-resolution  $^{13}\text{C}$  n.m.r. in the solid state can approach the sensitivity and resolution of liquid spectra by employing the techniques of high-power proton decoupling<sup>1,2</sup>, cross-polarization (CP)<sup>3,4</sup> and magic-angle sample spinning (MAS)<sup>5,6</sup>. Linewidths, however, are typically 10 to 100 times broader<sup>7</sup> than are found in solution-state spectra. In some cases, spectra of solid polymers are more informative<sup>5,8</sup> because different conformations present in the solid, which are motionally averaged in solution, can be resolved. One example is the chemical shift difference between the crystal and non-crystal components in polyethylene (PE), explained, at least partially, in terms of *trans* and *gauche* conformational effects<sup>9</sup>.

The poly(oxetanes), with general formula  $[-\text{CH}_2-\text{CR}_1\text{R}_2-\text{CH}_2-\text{O}]_n$ , where  $\text{R}_1$  and  $\text{R}_2$  are hydrogen atoms or alkyl groups, are of special interest because of crystal polymorphism. While the C–O bonds are always in the *trans* conformation (this corresponds to the C–C–O–C atomic sequence), the C–C bonds can be either *trans* or *gauche*. Three possibilities,  $T_4$ ,  $T_3G$  and  $T_2G_2$ , have been found in the crystalline structure of unsubstituted poly(oxetane) (PTO)<sup>10–12</sup> and in poly(3,3-dimethyloxetane) (PDMO)<sup>13</sup>, although the  $T_4$  structure has only been observed in the presence of external stresses<sup>12,13</sup> or in a hydrated crystal structure<sup>11</sup>.

The influence of crystallization conditions on the conformation of the crystal structure of these two polymers crystallized from the relaxed melt state has been previously reported<sup>14</sup>. PTO normally crystallizes with the  $T_2G_2$  conformation but PDMO will crystallize with either the  $T_3G$  or  $T_2G_2$  conformation, depending on the crystallization temperature. The relative stabilities of these polymorphs have also been studied by different techniques<sup>15,16</sup>. Moreover, the  $T_3G$  conformation in PTO has been obtained recently when the polymer is

crystallized from the quenched state<sup>17</sup>. In this case, the two modifications are present in proportions depending on isothermal crystallization temperature or heating rate<sup>17</sup>.

This study focuses on correlating MAS  $^{13}\text{C}$  solid-state n.m.r. spectra with different crystalline chain conformations in the cited poly(oxetanes).

## EXPERIMENTAL

The  $^{13}\text{C}$  n.m.r. spectra were obtained using a Bruker CXP200 spectrometer<sup>18</sup> operating at a static field of 4.7 T. The magic-angle sample spinning probe was manufactured by Doty Scientific Inc.<sup>18</sup> and employs a double air-bearing design. The aluminium oxide rotors have poly(chlorotrifluoroethylene) end caps which give no signal when cross-polarization (CP) techniques with phase alternation<sup>19</sup> are employed. Only in the  $(90^\circ-\tau)_x$  sequence does an end cap resonance appear, but this resonance does not interfere since it is very weak, very broad, and its maximum is downfield from the region of interest. The r.f. field strengths used for decoupling and cross-polarization ranged between 60 and 75 kHz. All cross-polarization times used were 1 ms. A 76 ms decoupling period was used for signal observation in the CP experiments, and 38 ms in the  $(90^\circ-\tau)_x$  ones. Because of the quite narrow signals (about 0.4 ppm, even less for the quaternary carbons in the crystal), a trapezoidal apodization was applied to the free induction decays at the 50 ms point in the CP experiments and at the 32.5 ms points in the  $(90^\circ-\tau)_x$  experiments. Even after apodization, some ringing is still observed for certain resonances.

Chemical shifts were measured by substitution using adamantane in a separate rotor as the reference. The high-field resonance of adamantane was taken to be 29.50 ppm<sup>20</sup>. Thus, the chemical shift differences for a given oxetane are very accurate, but the absolute accuracy of the shifts is probably  $\pm 0.4$  ppm.

The synthesis and characterization of the polymer fractions of PTO and PDMO have been given elsewhere<sup>14</sup>. These samples, crystallized for a long time at room temperature (HT preparations), were loaded into the rotors, after which the first set of data was taken. To obtain the low-temperature forms (LT preparations) of the two polymers, the samples were initially melted at 90°C inside the rotors. For PTO, the sample was then quenched in powdered dry ice, after which it was put in an isopropanol–dry ice bath at –55°C for about 20 min. The temperature was then raised slowly to 0°C and held for several hours. A later annealing for two days was done at 9°C before signal observation at 21°C. The low-temperature form of PDMO was prepared by crystallization from the melt at –5°C for one night.

## RESULTS AND DISCUSSION

The CP–MAS spectra of the two PTO preparations are seen in Figure 1 (spectra A and C). The top spectrum corresponds to the sample crystallized from the melt for a long time at room temperature, where only the  $T_2G_2$  modification is formed, and the second (spectrum C) is that of the sample crystallized at low temperature from the quenched state. In order to locate the resonances belonging to the non-crystalline component, corresponding  $(90^\circ - \tau)_x$  experiments were performed (spectra B and D

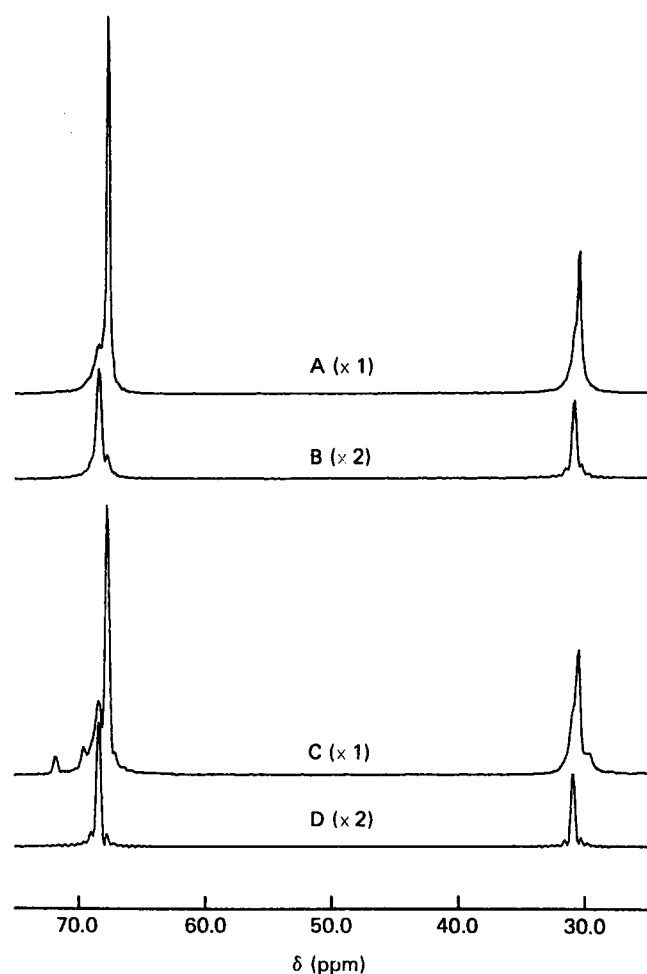


Figure 1 50 MHz solid-state  $^{13}\text{C}$  n.m.r. experiments for PTO: spectrum A, HT sample, CP experiment; B, HT sample,  $(90^\circ - 2\text{ s})_x$  experiment; C, LT sample, CP experiment; D, LT sample,  $(90^\circ - 2\text{ s})_x$  experiment. All spectra are normalized to the same total number of scans, but the  $(90^\circ - 2\text{ s})_x$  spectra are amplified by a factor of 2

Table 1 PTO chemical shifts<sup>a</sup> (in ppm)

	$T_2G_2$ conformation		$T_3G$ conformation	
	Crystal	Non-crystal	Crystal	Non-crystal
$\alpha$ -Methylenes	67.7	68.3	71.7 69.5	68.3
$\beta$ -Methylene	30.6	30.9	29.6	30.9

<sup>a</sup>Referenced to tetramethylsilane. Systematic error arising from reference by substitution is  $\pm 0.3$  ppm. Relative accuracy of any shift differences is  $\pm 0.15$  ppm. Corrections to the chemical shifts from second-order dipolar interactions<sup>33</sup> have not been made. To obtain the shift for the high-field limit, subtract 0.06 ppm for the crystalline methylenes. No correction is needed for the non-crystalline carbon sites

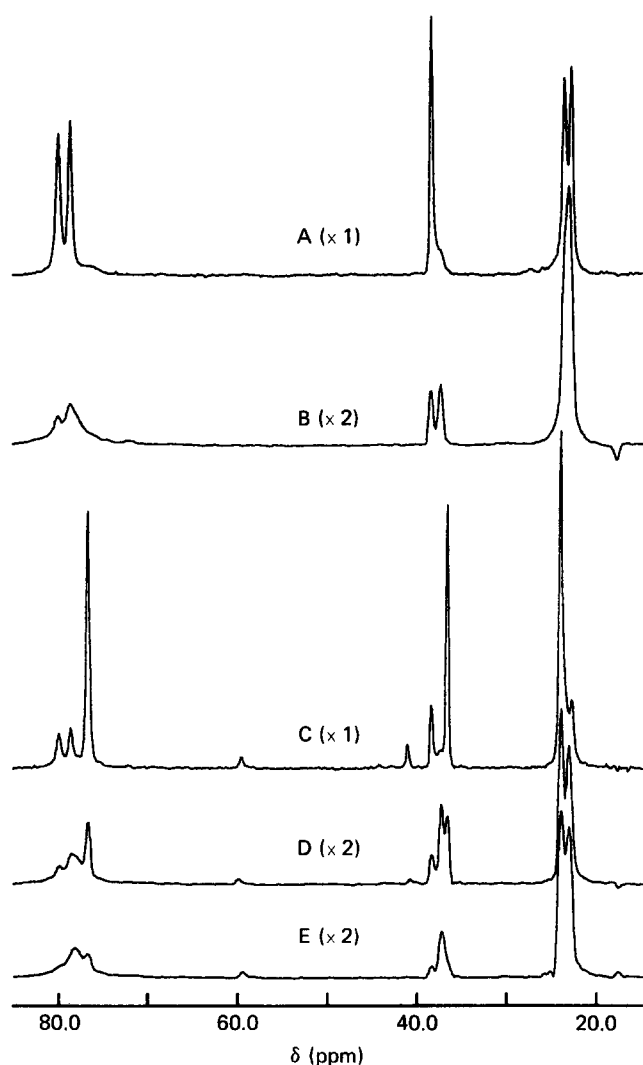
in Figure 1);  $\tau$  was chosen to be 2 s in order to emphasize the more mobile (non-crystalline) component whose longitudinal relaxation time  $T_1^C$  is expected to be much shorter than that of the crystal. From these experiments, the assignments of the different resonances for the higher-temperature preparation is straightforward, with the downfield shoulders of spectrum A in Figure 1 belonging to the non-crystalline component, comprising about 17% of the total signal of each carbon. The corresponding chemical shifts are shown in Table 1.

The crystallinity of the HT PTO sample can be deduced from the CP experiment if the CP enhancement factors,  $\epsilon_C$  and  $\epsilon_{NC}$ , for the methylene carbons in the crystalline and non-crystalline regions, respectively, are known. A value for  $\epsilon_{NC}$  may be obtained by comparing spectra A and B in Figure 1. The non-crystalline signals in the latter spectrum are fully relaxed on the basis of a  $(90^\circ - 15\text{ s})_x$  experiment. The value obtained for  $\epsilon_{NC}$  was 1.1. A knowledge of the crystalline enhancement factor  $\epsilon_C$  is required in order to determine the crystalline fraction. Since  $T_{1\rho}^H$  of the crystal is 26 ms (see Table 3), we can expect that  $\epsilon_C$  is near the theoretical enhancement of 4.0. We take  $\epsilon_C$  to be 3.5, which is typical of the methylene carbons in PE<sup>21</sup> whose crystalline protons have similar linewidth and relaxation characteristics. An  $\epsilon_C$  of 3.5 gives a 62% crystallinity for the HT preparation of PTO, in very good agreement with previous dilatometric values<sup>22</sup> and the proton results (see Table 3).

Returning to the LT PTO sample, it is clear from Figure 1 (spectrum C) that the dominant crystalline component has the high-temperature  $T_2G_2$  conformation and only about 15% corresponds to the low-temperature  $T_3G$  form. There are two reasons for this: first, the sample geometry is not adequate for effective quenching, and therefore the very fast crystallization of the  $T_2G_2$  conformation occurs; secondly, the low melting point (14°C<sup>17</sup>) of the  $T_3G$  component following quenching requires the annealing of the sample at temperatures around 0°C in order to raise this melting point to permit observation at room temperature. However, even with this annealing, a significant amount of  $T_2G_2$  conformation may be produced from the partial melting of the low-temperature form when the sample is warmed to 21°C in the  $^{13}\text{C}$  n.m.r. experiment. In any case, the pure crystalline spectrum of the  $T_3G$  modification can be obtained by subtracting from spectrum C a certain amount of spectra D and A. The corresponding chemical shifts for this modification are seen in Table 1. These results show that the  $\alpha$ -methylene resonance in the  $T_3G$  low-temperature modification exhibits a doublet while

this resonance is only a singlet in the  $T_2G_2$  high-temperature form. Thus, the two resonances in the  $T_3G$  form indicate inequivalent  $\alpha$ -methylene carbon sites within the unit cell. The most likely origin of this is the inequivalence of these methylenes within the same monomer unit. A modelling<sup>10</sup> of the  $T_3G$  conformational sequence shows, for example, that only one of the two  $\alpha$ -methylenes in the monomeric unit experiences a  $\gamma$ -gauche interaction<sup>23</sup>. These inequivalent interactions of the two  $\alpha$ -methylenes are no doubt principally responsible for the observed splitting.

This effect is more clearly seen in PDMO, where the most stable modification has a  $T_3G$  conformation. Spectrum A in Figure 2 corresponds to the CP experiment for the sample of PDMO crystallized at room temperature. In this spectrum, which is dominated by crystalline resonances, two doublets can be seen in the regions of the  $\alpha$ -methylenes and methyl substituents. The  $T_3G$  single chain conformation produces both inequivalent methyl and  $\alpha$ -methylene sites<sup>13</sup>. For the low-temperature preparation, whose dominant crystal form



**Figure 2** 50 MHz solid-state  $^{13}\text{C}$  n.m.r. experiments for PDMO: spectrum A, HT sample, CP experiment; B, HT sample,  $(90^\circ-2s)_x$  experiment; C, LT sample, CP experiment; D, LT sample,  $(90^\circ-15s)_x$  experiment; E, LT sample,  $(90^\circ-2s)_x$  experiment. All spectra are normalized to the same total number of scans, but the  $(90^\circ-\tau)_x$  spectra are amplified by a factor of 2. Sample spinning speed in the LT sample was limited to 1.8 kHz by rotor imbalance. Spinning sidebands from the methylene and methyl resonances appear near 42 and 59 ppm. The spurious signal near 18 ppm is from the carrier

**Table 2** PDMO chemical shifts<sup>a</sup> (in ppm)

	$T_2G_2$ conformation		$T_3G$ conformation	
	Crystal	Non-crystal	Crystal	Non-crystal
$\alpha$ -Methylenes	76.7	77.9	79.9 78.6	77.9
Quaternary	36.7	37.4	38.5	37.4
Methyls	24.1	23.1	23.6 23.0	23.1

<sup>a</sup> Referenced to tetramethylsilane. Systematic error arising from reference by substitution is  $\pm 0.3$  ppm. Relative accuracy of any shift differences is  $\pm 0.3$  ppm for the non-crystalline methylenes and  $\pm 0.15$  ppm for all the other resonances. Corrections to the chemical shifts from second-order dipolar interactions<sup>33</sup> have not been made. To obtain the shift for the high-field limit, subtract 0.06 ppm for the crystalline methylenes and 0.01 ppm for crystalline methyl carbons, although only the former correction makes sense in view of the accuracy of the data. No correction is needed for all the other resonances

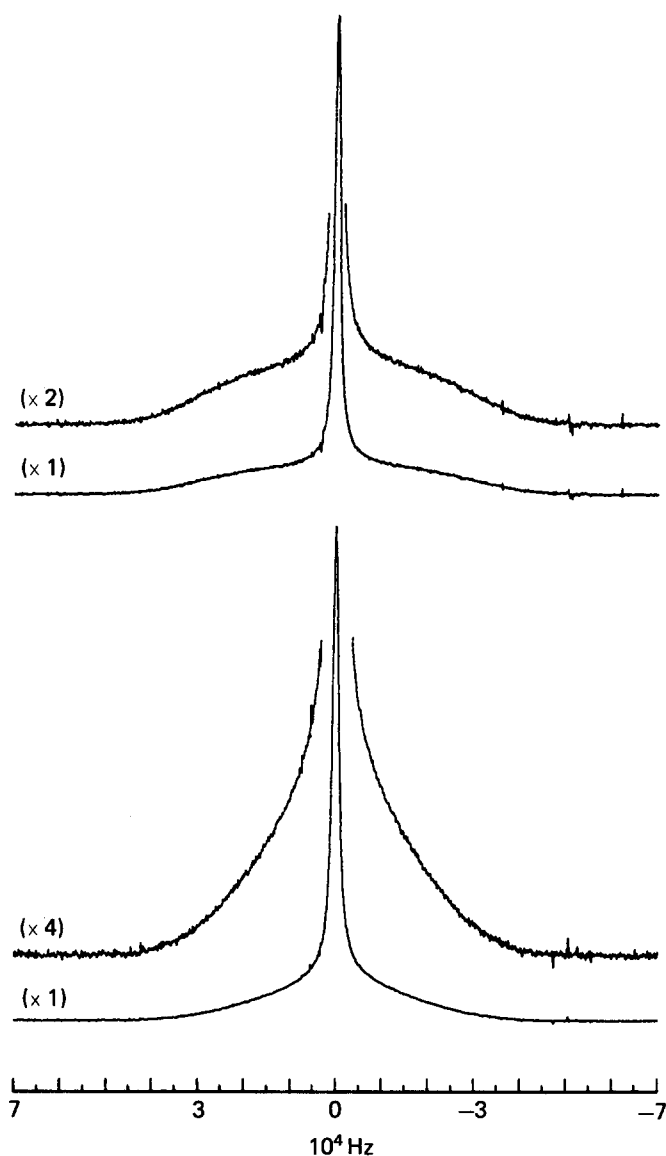
contains chains in the  $T_2G_2$  conformation, the CP spectrum is shown in spectrum C in Figure 2. Three main singlets for the crystalline resonances can be seen, corresponding to the three kinds of carbons in the monomeric unit. So, each carbon experiences only one kind of site. The  $T_3G$  crystalline form is present in this sample in a minor proportion due in part to the difficulty of selecting proper isothermal conditions. Nevertheless, chemical shifts for all the crystalline resonances are easily determined and these data are collected in Table 2. Thus, like in the case of PTO, the  $T_3G$  conformation gives rise to inequivalent  $\alpha$ -methylene sites (methyl inequivalence is also present in PDMO) while the  $T_2G_2$  conformation possesses only equivalent  $\alpha$ -methylene sites. The fact that the central  $\beta$ -carbon in both PTO and PDMO is not split in the  $T_3G$  conformation indicates that in both cases any variations in crystal packing from monomer unit to monomer unit at this carbon are negligible. This latter observation strongly supports the notion that the observed splittings occur because of the inequivalent sites within each monomer unit in the  $T_3G$  conformation.

In PDMO, however, the separation of the non-crystalline carbon resonances from the crystalline resonances is not as clear as it was in PTO, although a simplifying idea is that the non-crystalline resonances ought to be the same in the HT and LT samples. Only a weak shoulder in the quaternary carbon resonance, comprising about 10% of the total intensity for this carbon, can be clearly discerned in the CP experiment for the HT preparation of PDMO. At the same time, spectrum B in Figure 2 gives a good indication of the non-crystalline  $\alpha$ -methylene resonance, given that a small amount of doublet intensity from the crystalline resonance is also present. Identification of the non-crystalline methyl resonance requires a bit more care; however, its position may be determined quite accurately from spectra C, D and E in Figure 2, given that the ratio of non-crystalline to crystalline methyl intensity is much greater in spectra D and E compared with spectrum C. The general weakness of the non-crystalline resonances in the CP spectra of both Figures 1 and 2 prompted us to do a few proton experiments. We digress now to discuss them.

The proton data are summarized in Table 3. The equilibrium proton  $(90^\circ-5s)_x$  spectra are shown in Figure 3 for the high-temperature samples of PTO and PDMO. The main difference between these two spectra is the

Table 3 Parameters derived from solid-state proton experiments

Polymer	Sample	Crystallinity (%)	$T_1^H$ (s)	$T_1^H$ (ms) <sup>a</sup>		Linewidth (kHz)	
				Crystal	Non-crystal	Crystal	Non-crystal
PTO	HT	63	0.6	26	22	57	1.4
PDMO	HT	63	0.6	11	3.0	35	1.5
PDMO	LT	70	0.7	15	2.9	35	1.5

<sup>a</sup> $\gamma B_1/2\pi = 70$  kHz

**Figure 3** 200 MHz solid-state  $^1\text{H}$  n.m.r. lineshapes, normalized to the same total area, for the high-temperature samples of poly(oxetanes). Amplification factors are given. Upper spectra, PTO; lower spectra, PDMO. Small narrow spurious signals are visible under amplification in these spectra. These signals are due to the presence of coherent frequencies which become more noticeable when a very wide (2 MHz) filter bandwidth is used, as in the present case

shape of the broad crystalline resonance. This line is narrower in the case of PDMO, since 60% of the protons are associated with rotating methyls. Crystallinity can be measured quite easily from these spectra because the non-crystalline lineshape is so narrow compared with the crystalline resonance. The HT forms of both the PTO and PDMO samples have the same crystallinity, 63%. Crystallinities deduced from the proton spectra are in very good agreement with previous dilatometric

estimations<sup>22,24</sup> for the high-temperature modifications of these polymers. For the LT samples, comparison of the n.m.r. crystallinity with other methods is less meaningful because of the presence of the mixed crystalline phase. The extensive motional narrowing indicated by the non-crystalline resonance and the expected weak residual dipolar fields at the non-crystalline carbons explain the small values of  $\epsilon_{\text{NC}}$ . Since both HT forms also possess similar non-crystalline proton linewidths, the principal reasons for the weaker non-crystalline resonances (smaller  $\epsilon_{\text{NC}}$ ) observed in PDMO compared with PTO are: (1) the shorter  $T_1^H$  for the non-crystalline regions in PDMO compared with PTO, and (2) the probably larger local proton dipolar fields associated with methylene (PTO) carbons *versus* quaternary (PDMO) carbons.

Judging by the strong crystalline signals appearing in the methyl region of spectra B and E in Figure 2, it is apparent that these methyls are relaxing quite efficiently in 2 s. In order to explore whether the methyl resonance could be used as an alternative method for establishing crystallinity via the carbon spectra,  $T_1^C$  values for the crystalline carbons were measured<sup>25</sup> for just one sample, LT PDMO. The observed  $T_1^C$  values for the crystalline methyl, quaternary and methylene carbons were, respectively, 0.8 s, 26 s and 62 s. This accounts for the large contribution of the crystalline methyl resonance in spectra D and E of Figure 2 and probably in spectrum B as well.

The  $T_1^C$  values for the quaternary and methylene carbons merit additional comment. First, about 15% of the intensity in each of these lines relaxes with a  $T_1^C$  of a few seconds. This may be due to chains near the crystal/non-crystal interface. Secondly, the fact that the  $T_1^C$  of the methylene carbon is larger than that of the quaternary carbon very probably indicates that  $^{13}\text{C}$ - $^{13}\text{C}$  spin exchange with the methyl carbons is an important effect<sup>26</sup>, particularly for the quaternary carbon. Dipolar relaxation from bonded protons would be the logical mechanism determining the intrinsic  $T_1^C$  values; dominance of this mechanism would imply that the quaternary carbon possesses the longer  $T_1^C$ . The stronger  $^{13}\text{C}$ - $^{13}\text{C}$  spin exchange for the quaternary carbon compared with the methylene carbon is most likely a result of its narrow undecoupled resonance width compared with the methylene resonance<sup>27</sup>.

For the LT PDMO sample, the methyl resonance in spectrum D of Figure 2 represents a fully relaxed state for both the crystal and non-crystal methyl resonances; therefore, a deconvolution of this line into its crystalline and non-crystalline components should give the true crystallinity. However, the polymorphic character of the LT sample (76%  $T_2G_2$  phase, 24%  $T_3G$  phase, from spectrum C in Figure 2) complicates the deconvolution of the methyl signal in spectrum D in Figure 2. Taking account of the overlap of the non-crystalline methyl resonance with the HT crystalline methyl resonance, a

crystallinity of about 65% can be calculated for this LT preparation of PDMO, compared with the 70% obtained from proton experiments (see Table 3). Some error may be involved in the complicated procedure of deconvolution due to the presence of HT form.

Since  $T_1^C$  data were not taken on the HT PDMO sample and since all methyl resonances have a much more severe overlap, the crystallinity of this sample was checked via the  $^{13}\text{C}$  spectra by measuring the non-crystalline enhancement factor. A value of  $\epsilon_{\text{NC}} = 0.5$  was obtained for the quaternary resonance, which resonance presents the best resolved non-crystalline component. This value leads to a crystallinity of 56% for the HT PDMO sample if it is assumed, as for PTO, that  $\epsilon_{\text{C}} = 3.5$ . This determination becomes less precise as  $\epsilon_{\text{NC}}$  gets smaller. Yet that value of the crystallinity compares fairly well with the proton results of Table 3 as well as previous dilatometric determinations<sup>24</sup>. The proton determination of crystallinity, however, is the superior n.m.r. method in this case.

In conclusion, it has been shown that several crystallinity determinations from the solid-state n.m.r.  $^1\text{H}$  and  $^{13}\text{C}$  spectra give results in good agreement with dilatometric calculations. Proton determinations are very straightforward and accurate.  $^{13}\text{C}$  methods are not as precise but are still possible. When methyls are present, and when the methyl resonance may be properly deconvoluted, a  $(90^\circ - \tau)_x$  experiment with a  $\tau$  value probably less than 10 s can be used directly to obtain crystallinity. Otherwise, crystallinity in these kinds of samples, where the glass transition temperature is less than the n.m.r. measurement temperature<sup>14</sup>, may be calculated on the basis of a knowledge of the CP enhancement factors along with lineshape deconvolution.

One would like to extract some information from the results in Tables 1 and 2 about the magnitude of the  $\gamma$ -gauche effect. This interaction has been invoked to explain shifts between stereoisomers in polymers of varying tacticity<sup>28,29</sup> or as a possible contribution to the shift between the crystal and non-crystal signals in the solid-state  $^{13}\text{C}$  n.m.r. spectrum of PE<sup>9</sup>. CP-MAS spectra have been considered useful in elucidating the size of the  $\gamma$ -gauche effect. For example, in the solid-state  $^{13}\text{C}$  n.m.r. spectrum of syndiotactic polypropylene<sup>30</sup>, the methylene resonance is a doublet having an 8 ppm separation. This polymer crystallizes in an involuted helix<sup>31</sup> that gives rise to two types of methylenes, one having two and the other zero  $\gamma$ -gauche interactions. The inequivalence in this case is assigned to methylenes in two consecutive monomer units. If this 8 ppm splitting is interpreted solely in terms of the  $\gamma$ -gauche effect, then a single  $\gamma$ -gauche interaction between methylenes produces a 4 ppm shift. However, in the  $T_3G$  conformation of poly(oxetanes) the two methylenes in the monomer unit experience one and zero  $\gamma$ -gauche interactions with an oxygen. The observed doublet splitting for the  $\alpha$ -methylenes in this conformation is only 2.2 ppm in the case of PTO and 1.3 ppm in PDMO. In these splittings there is not only the influence of the  $\gamma$ -gauche effect but also possible crystal packing differences which may produce shifts of this order of magnitude, as was shown in the case of n-alkanes<sup>32</sup>. For example, the  $T_2G_2$  and  $T_3G$  crystalline forms in either PTO or PDMO possess  $\beta$ -carbon resonances which differ by 1–2 ppm in spite of the fact that this carbon experiences no  $\gamma$ -gauche interactions. These shifts could be due to crystal packing or possible small changes in

bond geometries for the isolated molecule. A similar shift (about 2 ppm) is observed between  $\alpha$ -methylene carbons having the same  $\gamma$ -gauche interactions: in the  $T_3G$  crystal form, one  $\alpha$ -methylene carbon (presumably identified with the upfield doublet component), and in the  $T_2G_2$  form, both  $\alpha$ -methylene carbons experience one  $\gamma$ -gauche interaction. Again, the reason for the shift is not apparent; moreover, the shift is similar to the observed splittings. Therefore, we are not inclined to attribute these splittings of the  $\alpha$ -methylenes entirely to the  $\gamma$ -gauche effect with an oxygen atom; at the same time, if this  $\gamma$ -gauche effect is present or even dominant, the shifts produced seem smaller than for a C–C  $\gamma$ -gauche interaction<sup>23,28</sup>.

The principal conclusion from these results is that the inequivalent sites within the monomer unit known to be associated with the  $T_3G$  conformation are evidenced by the splitting of the  $\alpha$ -methylene resonance. At the same time, the equivalence of these carbons in the  $T_2G_2$  conformation is evidenced by a single resonance. The singlet character of the  $\beta$ -carbon resonance is cited as further strong evidence that the observed inequivalence of the  $\alpha$ -methylene carbons in the  $T_3G$  form arises within each monomer unit, rather than between different monomer units in the unit cell. Therefore, the  $T_3G$  conformation in symmetrically substituted poly(oxetanes) should be easily distinguished from the  $T_2G_2$  conformation by  $^{13}\text{C}$  n.m.r. in the solid state. Thus,  $^{13}\text{C}$  n.m.r. will be useful in the determination of crystal structures in new symmetrically substituted poly(oxetanes). Asymmetric substitution can cause further splittings and possible additional effects due to tacticity considerations.

## ACKNOWLEDGEMENT

One of us (EP) wishes to acknowledge the Research Council of Spain (CSIC) for the award of a research grant, which supported this work at the National Bureau of Standards.

## REFERENCES

- 1 Pines, A., Gibby, M. G. and Waugh, J. S. *J. Chem. Phys.* 1973, **59**, 569
- 2 Sarles, L. R. and Cotts, R. M. *Phys. Rev.* 1958, **111**, 853
- 3 Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* 1972, **8**, 1
- 4 Lowe, I. J. *Phys. Rev. Lett.* 1959, **2**, 85
- 5 Schaefer, J., Stejskal, E. O. and Buchdahl, R. *Macromolecules* 1975, **8**, 291
- 6 Garroway, A. N., Moniz, W. B. and Resing, H. A. *Prepr. Div. Org. Coatings Plastics Chem.* 1976, **36**, 133
- 7 VanderHart, D. L., Earl, W. L. and Garroway, A. N. *J. Magn. Reson.* 1975, **44**, 361
- 8 Möller, M. *Adv. Polym. Sci.* 1985, **66**, 59
- 9 Earl, W. L. and VanderHart, D. *Macromolecules* 1979, **12**, 762
- 10 Tadokoro, H., Takahashi, Y., Chatani, Y. and Kakida, H. *Makromol. Chem.* 1967, **109**, 96
- 11 Kakida, H., Makino, D., Chatani, Y., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1970, **3**, 569
- 12 Takahashi, Y., Osaki, Y. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1152
- 13 Takahashi, Y., Osaki, Y. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1863
- 14 Pérez, E., Gomez, M. A., Bello, A. and Fatou, J. G. *Colloid Polym. Sci.* 1983, **261**, 571
- 15 Pérez, E., Fatou, J. G., Bello, A., Merino, J. C., Pastor, J. M. and deSaja, J. A. *Eur. Polym. J.* 1985, **21**, 449
- 16 Merino, J. C., Pastor, J. M., deSaja, J. A., Pérez, E., Bello, A. and Fatou, J. G. *Makromol. Chem.* 1985, **186**, 1731
- 17 Pérez, E., Fatou, J. G. and Bello, A. to be published

- 18 Certain commercial companies are named in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NBS
- 19 Stejskal, E. O. and Schaefer, J. J. *Magn. Reson.* 1975, **59**, 569
- 20 Earl, W. L. and VanderHart, D. J. *Magn. Reson.* 1982, **48**, 35
- 21 VanderHart, D. L. and Khoury, F. *Polymer* 1984, **25**, 1589
- 22 Pérez, E., Bello, A. and Fatou, J. G. *Colloid Polym. Sci.* 1984, **262**, 605
- 23 Tonelli, A. E. *Macromolecules* 1978, **11**, 565
- 24 Pérez, E., Fatou, J. G. and Bello, A. *Colloid Polym. Sci.* 1984, **262**, 913
- 25 Torchia, D. A. *J. Magn. Reson.* 1978, **30**, 613
- 26 Virlet, J. and Ghesquiers, D. *Chem. Phys. Lett.* 1980, **73**, 323
- 27 VanderHart, D. L. and Garroway, A. N. *J. Chem. Phys.* 1979, **71**, 2773
- 28 Tonelli, A. E. and Schilling, F. C. *Acc. Chem. Res.* 1981, **14**, 233
- 29 Schilling, F. C. and Tonelli, A. E. *Macromolecules* 1986, **19**, 1337
- 30 Harris, R. K., Packer, K. J. and Say, B. J. *Makromol. Chem.* 1981, Suppl. **4**, 117
- 31 Corradini, P., Natta, G., Ganis, P. and Temussi, P. A. *J. Polym. Sci. C* 1967, 2477
- 32 VanderHart, D. L. *J. Magn. Reson.* 1981, **44**, 117
- 33 VanderHart, D. L. *J. Chem. Phys.* 1986, **84**, 1196