

Reply to Comment on “²⁷Al Multiple-Quantum Magic Angle Spinning NMR Study of the Thermal Transformation between the Microporous Aluminum Methylphosphonates AlMePO-β and AlMePO-α”

Steven P. Brown,[†] Sharon E. Ashbrook,^{‡,§} and Stephen Wimperis^{*,§}

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany; Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom; and School of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, United Kingdom

Received: April 13, 1999

The Comment on “²⁷Al Multiple-Quantum Magic Angle Spinning NMR Study of the Thermal Transformation between the Microporous Aluminum Methylphosphonates AlMePO-β and AlMePO-α” is a response to a recent article in which we apply the ²⁷Al multiple-quantum magic angle spinning (MQMAS) NMR experiment to the study of aluminum methylphosphonates.¹ Apart from our main aim of demonstrating the excellent resolution that can be achieved with a five-quantum version of this experiment, another conclusion of this article was that our NMR results on a sample where the thermal transformation from the β to the α polymorph was interrupted before completion “do not appear to support the proposition of a topotactic reconstructive transformation.” This mechanistic proposition has recently been made, independently, by both Carter et al.² and by Maeda et al.,³ although we were not aware of the latter work³ at the time we prepared our article. Our choice of words (quoted above) was deliberate and careful as we were (and still are) not in a position to comment on the validity of the non-NMR evidence presented by Carter et al. and by Maeda et al. in support of their proposed mechanism. It would, therefore, be wrong to read our article¹ as an attempt to disprove the proposition of a topotactic reconstructive transformation for the thermal transformation of AlMePO-β to AlMePO-α.

The AlMePO samples were provided for us by Dr. V. J. Carter of the University of St. Andrews, Scotland, and were prepared as described by Carter et al.² The Comment is correct that our AlMePO-β sample was as-synthesized and contained dioxane and that, as a result, our physical mixture of AlMePO-α and AlMePO-β also contained dioxane; in contrast, the sample resulting from the interrupted thermal transformation probably did not contain dioxane as this would have been removed during the early stages of heating. This is, therefore, a possible explanation of the difference we observed in the five-quantum ²⁷Al MAS NMR spectra of the two samples.

The evidence presented in the Comment and elsewhere⁴ of significant changes in the ²⁷Al MAS NMR spectra as a result

of dioxane removal is open to question, however. For example, Figure 2 of the Comment shows that the entire (composite) tetrahedral-region ²⁷Al line shape shifts upfield (by ~0.5 ppm) in a uniform manner when dioxane is removed. To us, this small shift suggests (if reproducible) a change in bulk susceptibility upon removal of dioxane rather than any difference in mean Al–O–P angles. In contrast, in our high-resolution MQMAS results (Figure 6b,d of ref 1) only one of the three ²⁷Al peaks resolved in the tetrahedral region of the spectrum appears at higher field after heating.

Apart from this possible overall upfield shift of the (composite) tetrahedral-region ²⁷Al line shape, Figure 2 of the Comment also shows that there is a very small change in this line shape upon removal of dioxane. However, this composite line shape has been shown to consist of three second-order broadened constituent line shapes corresponding to the three crystallographically distinct tetrahedrally coordinated Al atoms in the unit cell.^{1,5} The presence of this second-order quadrupolar broadening has the following consequences: (a) the three constituent ²⁷Al line shapes overlap each other to a considerable extent in the MAS spectrum (i.e., the spectrum is not “resolved”); (b) the number of local maxima (i.e., “peaks”) in the overall MAS line shape cannot be equated with the number of Al sites; and (c) the isotropic shifts of the centers of gravity of the constituent ²⁷Al line shapes depend on both chemical shifts and second-order quadrupolar shifts; unless a correction is made for this second effect, any “chemical shifts” measured directly from ²⁷Al MAS NMR spectra will not be accurate and their detailed interpretation (for example, in terms of mean Al–O–P angles⁴) will be of no value. The two “peaks” in the ²⁷Al MAS spectrum of AlMePO-α in Figure 2 of the Comment are a good example of point (b); to us, as expected from the crystal structure, this appears to be a single second-order broadened quadrupolar MAS line shape. We believe, therefore, that the question of the exact nature of the small line shape change that occurs upon removal of dioxane and whether this explains the differences between Figure 6, c and d, of ref 1 can only be resolved (quite literally) if either the MQMAS experiment or much higher magnetic field strengths are used to suppress the second-order quadrupolar broadening.

In conclusion, the explanation of our five-quantum ²⁷Al MAS NMR spectra of AlMePO samples suggested in the Comment is certainly promising. In our earlier work,¹ however, again using carefully and deliberately chosen language, we noted that “further work is necessary to resolve this apparent contradiction.” We still believe this to be the case.

Our failure to cite refs 3 and 4 in our earlier work was a regrettable oversight on our part.

References and Notes

- (1) Brown, S. P.; Ashbrook, S. E.; Wimperis, S. *J. Phys. Chem. B* **1999**, *103*, 812.
- (2) Carter, V. J.; Wright, P. A.; Gale, J. D.; Morris, R. E.; Sastre, E.; Perez-Pariente, J. *J. Mater. Chem.* **1997**, *7*, 2287.
- (3) Maeda, K.; Sasaki, A.; Watanabe, K.; Kiyozumi, Y.; Mizukami, F. *Chem. Lett.* **1997**, 879.
- (4) Maeda, K.; Kiyozumi, Y.; Mizukami, F. *J. Phys. Chem. B* **1997**, *101*, 4402.
- (5) Rocha, J.; Lin, Z.; Fernandez, C.; Amoureux, J. P. *Chem. Commun.* **1996**, 2513.

* To whom correspondence should be addressed. Fax: +44-1392-263434. E-mail: s.wimperis@exeter.ac.uk.

[†] Max-Planck-Institut für Polymerforschung.

[‡] University of Oxford.

[§] University of Exeter.