The Detection of Preferred Conformations in Oligomers of Methyl Methacrylate in Solution by ^{1}H N.M.R. 2D-Correlation Spectroscopy

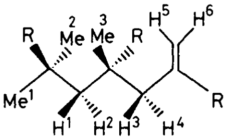
Paul Cacioli, David G. Hawthorne, Stanley R. Johns,* David H. Solomon, Ezio Rizzardo, and Richard I. Willing
Division of Applied Organic Chemistry, CSIRO, G.P.O. Box 4331, Melbourne, 3001, Australia

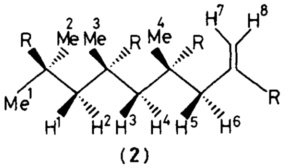
The observation of four bond, extended 'W' pathway, ^{1}H,^{1}H connectivities between specific protons of the methylene and methyl groups in methyl methacrylate oligomers (**1**)—(**6**) by ^{1}H n.m.r. 2D-correlation spectroscopy indicates preferred conformations in solution for chains composed of methyl methacrylate units.

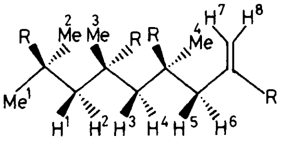
The value of model oligomers in the study of the stereochemical configuration of polymer chains has been demonstrated in several recent publications.[1—3] We now present data which show that the methyl methacrylate (MMA) oligomers (**1**)—(**6**), with the relative configurations shown, have preferred conformations in solution and we suggest that similar conformational preferences occur in poly(methyl methacrylate).

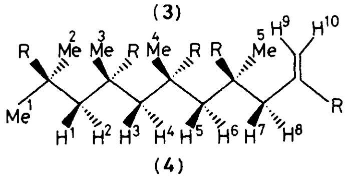
Four bond, extended 'W' pathway, scalar couplings are commonly observed in saturated, cyclic compounds with fixed configurations, even when freely rotating methyl groups are involved.[4] The 2D-correlation spectroscopy (COSY) technique is the method of choice for detecting ^{1}H,^{1}H connectivities, especially long-range connectivities where the magnitude of the scalar coupling is less than the linewidth of the signals.

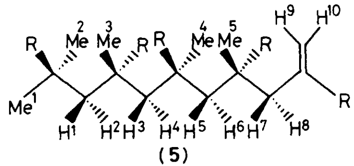
We have synthesized and separated the MMA oligomers (**1**)—(**6**)† and proved their structures by 2D-COSY. The geminal AB proton signals of the individual methylene groups are assigned from appropriate off-diagonal peaks, as observed in the spectrum of the stereoisomer (**2**), the *meso*-tetramer in polymer nomenclature[5] (Figure 1). The four bond, extended 'W' pathway, ^{1}H,^{1}H connectivities 4-H ⟷ 3-Me and 4-H ⟷ 4-Me in (**2**), shown by off-diagonal peaks in Figure 1, and 3-H ⟷ 4-Me and 4-H ⟷ 3-Me in the stereoisomer (**3**), confirm the configurations at the two asymmetric centres in each compound and indicate strongly preferred conformations in these regions of the molecules. Similar four bond, extended

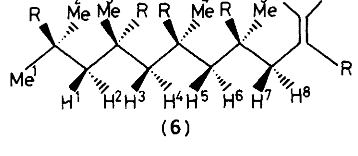

(**1**)


(**2**)


(**3**)


(**4**)


(**5**)


(**6**)

R = CO_2Me

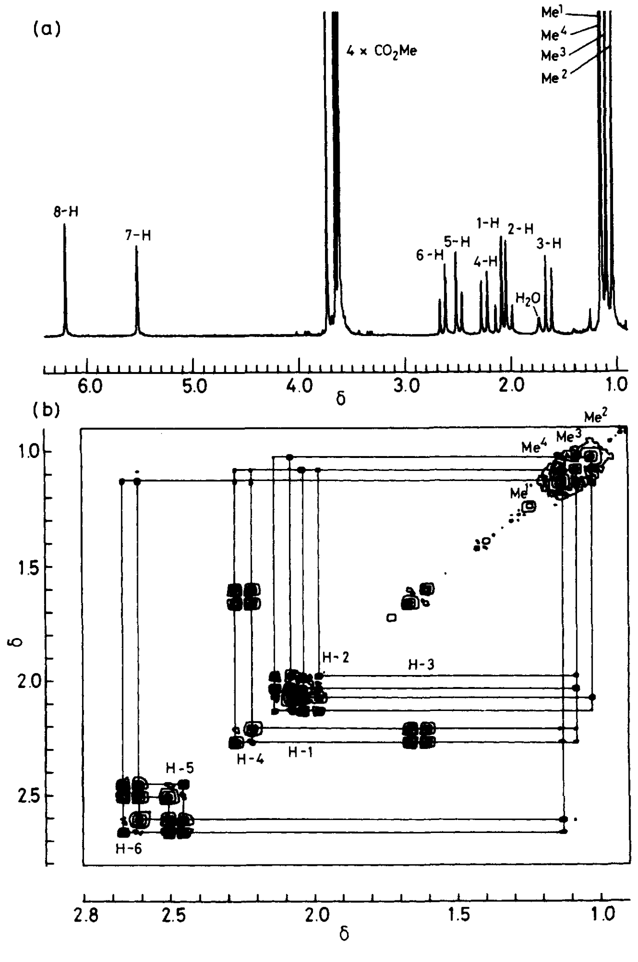


Figure 1. (a) 250 MHz ^{1}H n.m.r. spectrum of oligomer (**2**) in $CDCl_3$. (b) Partial 2D-COSY spectrum of oligomer (**2**) in $CDCl_3$.

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† Prepared by free radical polymerization using cobalt(II) tetraphenylporphyrin as chain transfer agent (N. S. Enikolopyan, B. R. Smirov, G. V. Ponomarev, and I. M. Belgovskii, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 879) and separated by h.p.l.c. on silica.

Table 1. 2D-COSY derived ^{1}H,^{1}H connectivities in MMA oligomers (**1**)—(**6**).

Compound	Connectivities
(**1**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 4-H ⟷ 3-Me, 2-H ⟷ 3-Me 1-H ⟷ 2-Me.
(**2**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 5-H ⟷ 6-H, 6-H ⟷ 4-Me, 4-H ⟷ 4-Me, 4-H ⟷ 3-Me, 2-H ⟷ 3-Me, 1-H ⟷ 2-Me.
(**3**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 5-H ⟷ 6-H, 5-H ⟷ 4-Me, 3-H ⟷ 4-Me, 4-H ⟷ 3-Me, 2-H ⟷ 3-Me, 1-H ⟷ 2-Me.
(**4**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 5-H ⟷ 6-H, 7-H ⟷ 8-H, 7-H ⟷ 5-Me, 6-H ⟷ 4-Me, 5-H ⟷ 5-Me, 4-H ⟷ 4-Me, 4-H ⟷ 3-Me, 2-H ⟷ 3-Me, 1-H ⟷ 2-Me.
(**5**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 5-H ⟷ 6-H, 7-H ⟷ 8-H 8-H ⟷ 5-Me, 6-H ⟷ 5-Me, 5-H ⟷ 4-Me, 4-H ⟷ 3-Me, 3-H ⟷ 4-Me, 2-H ⟷ 3-Me, 1-H ⟷ 2-Me.
(**6**)	1-H ⟷ 2-H, 3-H ⟷ 4-H, 5-H ⟷ 6-H, 7-H ⟷ 8-H, 7-H ⟷ 5-Me, 5-H ⟷ 5-Me, 5-H ⟷ 4-Me, 4-H ⟷ 3-Me, 3-H ⟷ 4-Me, 2-H ⟷ 3-Me, 1-H ⟷ 2-Me.

'W' pathway, connectivities 6-H ⟷ 4-Me and 1-H ⟷ 2-Me in (**2**) and 5-H ⟷ 4-Me, 2-H ⟷ 3-Me, and 1-H ⟷ 2-Me in (**3**) also indicate preferred conformations about the terminal groups. Although the magnitudes of the averaged, four bond couplings are not quantified, the absence of detectable ^{1}H,^{1}H connectivities from other conformations with extended 'W' pathways, such as 2-H ⟷ 1-Me in (**2**) or (**3**) after 60° rotations of the terminal groups, indicates that the contribution to the averaged couplings from such conformations are small. We believe, therefore, that the conformations shown are highly preferred.

2D-COSY derived connectivities for compounds (**1**)—(**6**), summarized in Table 1, establish the configurations at the asymmetric centres in each oligomer and indicate the conformational preferences in solution as shown.

We know of no other instance, in the absence of hydrogen bonding, where acyclic compounds have been shown to have such marked conformational preferences. These findings should have particular relevance to studies of the behaviour of poly(methyl methacylate) in solution.

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