WILLIAMS REPLIES—The biggest weakness of the study by Wilcox and Scherrer is immediately apparent. In subdividing the keydates according to their excursion, Wilcox and Scherrer have allowed themselves freedom to select the data *a posteriori*. Despite the work of Hines and Halevy[1] there is no known physical reason for selecting the data in this manner. In this context, it must be remembered that the data has already been carefully selected, for example the wintertime, 500 or 300 mbar VAI is chosen since it exhibits the best result. Unfortunately, in the absence of a physical understanding this is one of the few ways in which we can progress. Indeed, I have been working along similar lines[2].

A lesser weakness has been pointed out by Hines and Halevy[1]. If one hypothesises that the 'signal' is the remnant of the 'noise' in the VAI dataset, then one might also expect the signal to increase as the noise increases. However, one would not expect the consistency claimed by Wilcox and Scherrer. A new point along these lines concerns the definition of the excursion. If the signal is real, then the strength of the signal can hardly depend on the meteorological noise after day 0 since then one would merely be correlating the signal with itself. Therefore, I would like to see the analysis repeated, this time selecting keydates according to the excursion before the start of the signal.

With regard to more minor points, I would like to see the results of the same analysis at 300 mbar; and how sensitive is Fig. 3 to a small change in x_s?

If the signal is real and does depend on the intrinsic variability of the atmosphere, then this is an important result which ought to have strong implications for the search for a mechanism. In this case the study of Wilcox and Scherrer should be taken further to answer some important questions. For example is there a critical excursion below which no effect occurs? Is there a proportionality between the excursion and the amplitude of the signal? (The winters 1968–71, which could be interpreted as 1967–71 in view of the 3-y average employed and the '1967' and '1972' results, seem to suggest this is not so.) Can the winter–summer asymmetry of the result be explained in this manner, since one could expect the excursion to be less in summer?

The simplest interpretation of the VAI–SSB effect still seems to be statistical chance. This belief has been reinforced by an interpretation of this effect in terms of the tropospheric energetics in the wavenumber domain[3].

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Anionic copolymerisation of episulphides with elemental sulphur

PENCZEK *et al.*[1] believe that the anionic copolymerisation of propylene sulphide (PS) with elemental sulphur gives the high-molecular weight polysulphide polymers $-CH_2-CH(CH_3)-S_x-$ (% S up to 90%, that is, $x = 12$). Nevertheless, PS mainly yields copolymers with $x \leq 2$ (refs 2, 3). We believe that this contradiction[1–3] is caused by the presence of residual sulphur in the PS copolymers[1], which can be detected in the elementary analysis and does not show up in the NMR spectra. This assumption is based on our experimental data[2] and also confirmed by ^{13}C NMR data[1] which indicate that PS copolymers with $x \leq 2$, and not polysulphide polymers with x up to 12 (ref. 1), are being formed. Indeed, polypropylene sulphide ($x = 1$) is characterised by the signals δ20.7 for CH_3, δ38.6 for CH_2 and δ41.0 and 41.2 for CH[4], whereas polypropylene disulphide ($x = 2$)[5] is characterised by the signals δ19.05 for CH_3, δ44.6 and 45.0 for CH_2 and δ46.0 and 46.4 p.p.m. for CH[6]. The spectra of PS copolymers with $2 > x > 1$ also have the signals of conjunctive units —SS—CH_2—$CH(CH_3)$—S—CH_2—$CH(CH_3)$—SS— at δ39.9 and 39.5 for CH, δ37.4 for CH_2 and δ19.4 p.p.m. for CH_3 (ref. 6). Therefore the increase in the intensity of signals 45.8, 45.6, 39.5, 39.1 and 19.4 p.p.m. with the increasing sulphur content in PS copolymers[1] are due to the increase in the amount of disulphide bonds ($x = 2$), and not polysulphide bonds ($x > 2$) as other signals in the spectra are absent (for example, CH_3 signal of trisulphide units should appear at δ18.1 p.p.m.[6]). It follows that the apparent values of $x = 2$ and 5 in the spectra of PS copolymers[1] conform to $x \leq 1.5$ and 1.7, respectively. Like the ^{13}C NMR data[1,2], ^1H NMR spectra of PS copolymers[2] correspond to that of PS polymers with a varying ratio of mono- and disulphide units[6].

We have shown previously[2,3] that the probability of a polysulphide polymer formation increases as the nucleophilic reactivity of episulphides decreases. Very reactive ethylenesulphide is predominantly converted into polyethylene sulphide ($x = 1$). Polysulphide polymers ($x > 2$) are mainly produced from a less reactive cyclohexene sulphide, isobutylene sulphide and trimethylethylenesulphide. The latter forms the copolymers with x up to 7 whose ^1H NMR spectra show a gradual downfield shift of proton signals as x is increased in the case of more reactive PS. The probability of homopolymerisation and formation of stable disulphide units increases as unstable polysulphide chains must split at hard reaction conditions[1]. The stereochemical effect of substituents and more mild copolymerisation conditions[2] apparently decrease the homopolymerisation rate of substituted episulphides and thereby increase the probability of their copolymerisation with sulphur as well as stabilise and restrict the participation of polysulphide chains (at least for $x \leq 5$) in nucleophilic splitting reactions because of the sterically hindered growing thiolate anions. Thus, despite these limitations, which can be overcome by using active forms of sulphur, inorganic polysulphides or UV irradiation[2], this method offers broad possibilities in the synthesis of polysulphide polymers[2,3].

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PENCZEK *ET AL.* REPLY—Aliev *et al.* have confirmed a general principle of anionic copolymerisability of elemental sulphur[1], including copolymers with various cyclic sulphides as described in our patent[2]. However, Aliev *et al.* assume that copolymers of propylene sulphide with elemental sulphur could have merely be solid solutions of polysulphide polymers $-CH_2-CH(CH_3)-S_x-$ with an average $\bar{x} < 2$ and elemental sulphur. This was based on their failure to prepare in their system copolymers of propylene sulphide with higher sulphur content, and on their interpretation of the ^{13}C-NMR spectra. However, great care must be taken with the interpretation of the NMR spectra of polysulphides, because we observed recently that the upfield signals can be caused by the presence of the low-molecular weight cyclic polysulphides. These products were removed from our polymers by an extensive extraction with boiling methyl alcohol (unreacted sulphur was removed in the same way)[3].

Had Aliev *et al.* attempted to repeat our experiments, leading to the true copolymers with high content of the built in sulphur, it would have become clear that, for example, a 50:50 mixture of polypropylene sulphide and elemental

0028–0836/79/350846—02$01.00