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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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R. E. Cais^{ab}; J. H. O'donnell^a

^a Chemistry Department, University of Queensland, Brisbane, Australia ^b Bell Telephone Laboratories, Murray Hill, New Jersey

To cite this Article Cais, R. E. and O'donnell, J. H.(1976) 'NMR Determination of the Microstructure of Polyvinyl Chloride Sulfone). II. ^{13}C -(^1H) Spectra', Journal of Macromolecular Science, Part A, 10: 5, 769 – 780

To link to this Article: DOI: 10.1080/00222337608061216

URL: <http://dx.doi.org/10.1080/00222337608061216>

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NMR Determination of the Microstructure of Poly(vinyl Chloride Sulfone). II. $^{13}\text{C}-\{^1\text{H}\}$ Spectra

R. E. CAIS* and J. H. O'DONNELL†

Chemistry Department
University of Queensland
Brisbane 4067, Australia

ABSTRACT

The $^{13}\text{C}-\{^1\text{H}\}$ NMR spectra of poly(vinyl chloride sulfone)s with macroscopic compositions corresponding to the ratio vinyl chloride (V):SO₂(S) = n from ca. 1 to 4 have been analyzed in terms of comonomer sequences and configurational placements. In the copolymer with $n \approx 1$, methylene and methine carbons in SVS sequences were resolved and were sensitive to "across SO₂" tacticity. No SVS sequences were observed in the copolymer with $n = 2.0$, confirming that it had a regular SVVS structure, which also showed a high "internal" stereosequence regularity. It was not possible to discriminate the methylene or methine carbon atoms in S(V)_nS sequences with $n \geq 2$.

*Present address: Bell Telephone Laboratories, Murray Hill, New Jersey 07974.

†To whom correspondence should be addressed.

INTRODUCTION

Vinyl chloride (VC) and sulfur dioxide will copolymerize by a free-radical mechanism to form a high molecular weight poly(vinyl chloride sulfone) [1-4]. The polymerization may be initiated by γ -irradiation or suitable chemical initiators, and the rate of copolymerization shows a very strong dependence on the comonomer composition.

The macroscopic composition of poly(vinyl chloride sulfone) may be conveniently expressed by the ratio n of vinyl chloride to SO_2 units in the chain. The value of n varies markedly with the polymerization temperature and on the comonomer composition in certain temperature and composition regions. It approaches a minimum value of 1 at low temperatures and low vinyl chloride concentration in the feed. At high temperatures and high vinyl chloride concentrations we have prepared poly(vinyl chloride sulfone)s with n in the range 2-85, i.e., approaching pure poly(vinyl chloride). This is in contrast to poly(olefin sulfone)s, which have a strictly alternating comonomer structure [5] with $n = 1.0$ for all comonomer compositions and all polymerization temperatures (below the appropriate ceiling temperature [6]) when prepared in the liquid phase.

The copolymerization of vinyl chloride and SO_2 does not obey first-order Markoff statistics (Lewis-Mayo copolymerization behavior) except as a limiting situation at low temperatures. Various models can be proposed for the mechanism of the propagation step(s) involving, for example, complex participation, penultimate unit effects, and depropagation reactions, in order to explain the experimentally observed relationships between copolymer composition and comonomer composition at different temperatures. However, it is not possible to distinguish between these models on the basis of macroscopic copolymer compositions alone. Therefore, additional information is essential. For this purpose comonomer sequence distributions are of great value and they are now experimentally accessible at least in suitable cases and for limited sequence lengths.

The present work was undertaken in an endeavor to elucidate the comonomer sequence distributions in poly(vinyl chloride sulfone)s prepared under different conditions and hence to confirm and possibly extend information derived from ^1H NMR spectral studies of poly(vinyl chloride- β , β - d_2 sulfone)s [4].

The ^{13}C - $\{^1\text{H}\}$ spectra of some poly(olefin sulfide)s have been reported [7, 8] and also the spectrum of poly(but-2-ene sulfone) [9]. It was found that the SO_2 groups caused substantial deshielding in the adjacent main-chain carbon positions. This present paper is the first report of the ^{13}C - $\{^1\text{H}\}$ spectra of variable-composition polysulfones.

EXPERIMENTAL

Poly(vinyl chloride sulfone)s were prepared by free radical copolymerization of liquid mixtures of vinyl chloride and sulfur dioxide. The polymerization was initiated by either cobalt-60 γ -irradiation or tert-butyl hydroperoxide/methanol [10, 11] as described in a previous paper [4]. Polymerization temperatures from -78 to $+46^\circ\text{C}$ and various comonomer compositions were used. The rate of copolymerization was very dependent on both of these variables. It decreased rapidly at high SO_2 concentrations, especially at higher temperatures, which limited the useful polymerization conditions. Copolymers with a low vinyl chloride content ($n < 2$) were very susceptible to dehydrochlorination on irradiation, on heating, or when dissolved in basic solvents such as dimethyl sulfoxide (DMSO) [4]. Therefore, these copolymers were usually prepared by chemical initiation, dried under vacuum at 30°C and dissolved in acetone or tetrahydrofuran (THF).

The details of the conditions used to prepare the copolymers for which NMR spectra are given in this paper are shown in Table 1. CCl_4 (3% v/v) was added to the comonomer mixtures for radiation-initiated polymerization at 30°C . This enhanced the initiation rate and minimized degradation by irradiation of the copolymer.

The ^{13}C spectra were obtained from 20% (w/v) solutions in perdeuterated acetone, THF, or DMSO at 60°C . This was the optimum temperature for satisfactory resolution and minimum decomposition of the copolymers. A Brüker HX-90 spectrometer was used with internal deuterium lock. The pulse recycle time was selected at 1.0 sec [cf. T_1 for methylene + 0.07 sec and T_1 for methine = 0.12 sec in poly(vinyl chloride)] in order to avoid saturation. Chemical shifts were measured relative to internal TMS.

TABLE 1. Details of Preparation of the Copolymers

n	$(x_{\text{VC}})_m$	Temp ($^\circ\text{C}$)	Initiator
1.1	0.50	-78	t-BuOOH
2.0	0.40 ^a	0	γ
2.0	0.80	0	γ
2.8	0.30	30	γ
3.9	0.70	30	γ

^aVinyl chloride- β, β - d_2 .

The copolymers with $n = 1$ and 2 were scanned for ca. 30 min (2000 scans), and the copolymers with higher vinyl chloride contents ($n \approx 3$ and 4) were scanned for ca. 15 hr (55,000-65,000 scans). The methyl carbon resonances for the solvents (deuterium coupled) are centered at 30.4 and 40.5 ppm for acetone and DMSO, respectively [12], and appear as the septuplet at high field in the spectra.

RESULTS AND DISCUSSION

Copolymers with $n \approx 1$

SVS Assignments*

The spectrum obtained from the copolymer with $n = 1.1$ in acetone is shown in Fig. 1. When this copolymer was dissolved in DMSO, dehydrochlorination proceeded rapidly during storage at room temperature and while the spectrum was being recorded. A major new resonance area then developed, which was

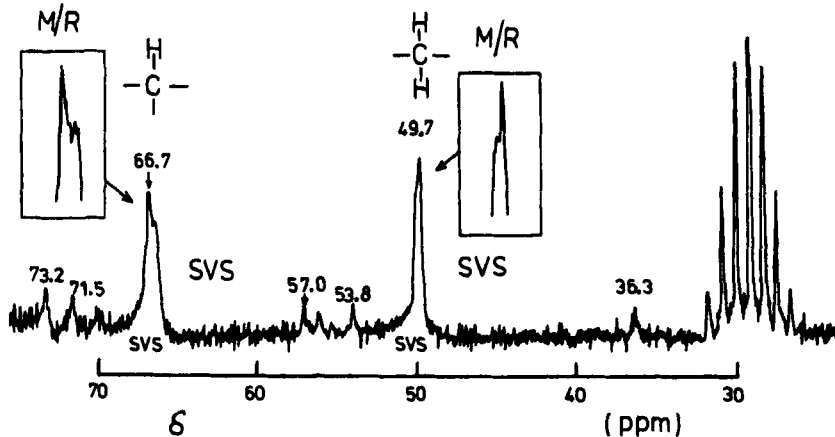


FIG. 1. Spectrum of poly(vinyl chloride sulfone) with $n = 1.1$ in acetone from 2000 scans.

*Abbreviations used in the sequence distributions are:- S = SO_2 unit, V = vinyl chloride unit, E = $-\text{CH}=\text{CH}-$ unit (ethene) formed by dehydrochlorination of a V unit.

centered at 142.3 ppm. This chemical shift is in good agreement with the chemical shifts of the olefinic carbon atoms in divinyl sulfone [13]. Therefore, this resonance can be assigned to SES triads.

When acetone was used as the solvent, dehydrochlorination was negligible during the time taken to collect the 2000 scans. The principal features of the spectrum in Fig. 1 are the two main peaks at 66.7 and 49.7 ppm, which are due to the methine and methylene carbon nuclei in SVS triads, respectively. The chemical shift of the methylene carbon is almost the same as that for the methine carbons in poly(but-2-ene sulfone) [9] as might be expected, while the methine carbon is shifted further downfield due to deshielding by the electro-negative chlorine substituent. Both resonances were sensitive to "across SO₂" tacticity (M and R). The ratio of the peaks in the doublets (the splitting was less for the methylene carbon, but can be observed on an expanded scale as shown in the insets) is 1.3, in agreement with the value obtained by ¹H NMR measurements on the partially deuterated copolymer. This confirms that there is a preferred steric pathway for the propagation step $\sim VS\cdot + V \rightarrow \sim VSV\cdot$ possibly via an association complex. However, without a study of model compounds, the peaks cannot be assigned to the particular isomers.

SVVS Assignments

Five small peaks are also observed in the spectrum in acetone of the copolymer with $n = 1.1$. These peaks have the chemical shifts shown in Fig. 1 and they can be attributed to the presence of a small proportion of SVVS tetrads.

Copolymers with $n \approx 2$

SVVS Assignments

The five small peaks in Fig. 1 are shown more clearly in Fig. 2A, which is the spectrum of the copolymer with $n = 2.0$. The positions of these peaks show only a slight solvent dependence.

When the methylene carbon was substituted with deuterium, the spectrum shown in Fig. 2B allows the methylene carbons to be assigned to the peaks at 55.3 and 35.5 ppm. These peaks are broadened and reduced in intensity in the partially deuterated copolymer, due to ¹³C-²H coupling (only ¹H was broad-band decoupled) and a reduced nuclear Overhauser enhancement factor.

There were no SVS sequences observable in these spectra (their position as observed in the copolymer with $n = 1.1$ is shown in Fig. 2A, in accord with our previous PMR results [4], which showed that the

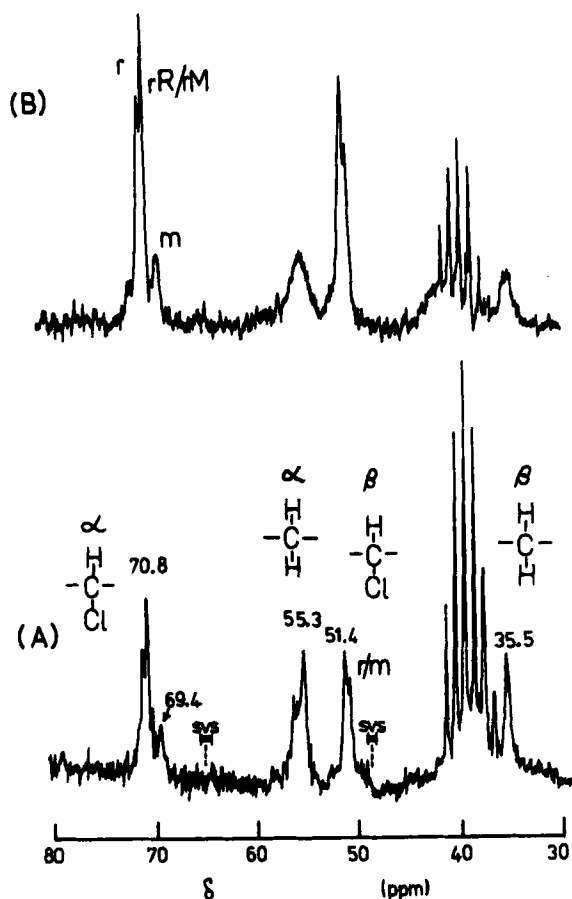


FIG. 2. Spectra of poly(vinyl chloride sulfone)s with $n = 2.0$ in DMSO prepared from (A) fully protonated vinyl chloride and (B) vinyl chloride- β, β - d_2 ; 2000 scans.

copolymer with $n = 2.0$ consists almost exclusively of SVVS sequences. The following assignments can be made for the copolymer with $n = 2.0$: α -sulfonyl methine at 71-69 ppm, α -sulfonyl methylene at 55.3 ppm, β -sulfonyl methine at 51.4 ppm and β -sulfonyl methylene at 35.5 ppm. Both α -sulfonyl resonances appear at lower field than those in SVS sequences, which might seem to be anomalous. However this is readily explained by a steric-compression shift [14], whereby

the normal sp^3 bond angles at carbon are distorted by steric interactions, which leads to greater screening at the nucleus. These steric interactions will arise from electrostatic-repulsion forces between chlorine substituents and the oxygen atoms on nearby sulfone groups. This strain will be somewhat relieved in the SVVS sequence compared to the SVS sequence, accounting for the approximate 5 ppm upfield shift of both ^{13}C nuclei in the latter sequence.

Fine Structure

The carbon resonances in SVVS sequences all show some fine structure, which cannot be attributed to neighboring sequence-length effects, due to the negligible proportion of sequences other than SVVS, and must therefore be due to tacticity effects.

Methine Carbon α to SO_2

This resonance (71-69 ppm) is more sensitive to tacticity than the β -sulfonyl methine (51 ppm), which is the reverse of the situation observed for the corresponding protons. This is probably because the C- SO_2 bond is most sensitive to the extent of steric strain in the two stereoisomers, whereas the proton in the α -sulfonyl position has a chemical shift dominated mainly by the sulfone group. A similar effect, i.e., a tacticity-sensitive proton being bonded to a tacticity-insensitive carbon, has been reported in poly(propene sulfide) [7]. The fine structure of the α -sulfonyl methine resonance is more clearly seen in the spectrum of the partially deuterated copolymer. (The concentration of the copolymer solution was 20% w/v for the methylene-deuterated copolymer and 12% w/v for the fully protonated copolymer.) The main peak (70.8 ppm) is split into a doublet and there is a second small peak to the high-field side of this resonance (69.4 ppm). This situation may be compared with the splitting of the resonances from α - and β -sulfonyl methine protons in SVVS sequences [4].

By analogy with the proton spectra, the peak at 70.8 ppm is assigned to the α -sulfonyl methine carbon in the r diad stereo-sequence and the one at 69.4 ppm to this carbon in the m diad stereo-sequence. The ratio r/m is 5.3 in the present case, comparing favorably with the value of 5.8 from the proton spectra. The peak assigned to the r diad clearly shows doublet splitting which is assigned to rR and rM "triad" stereosequences, although the individual assignments cannot be made. The ratio of these two peaks is 1.4, supporting the PMR results that "across- SO_2 " tactic diads are not equally probable. The ratio determined from the PMR spectrum of the copolymer prepared at $-78^\circ C$ was 1.3. It therefore appears that

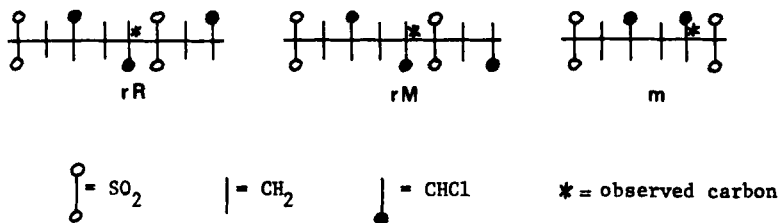


FIG. 3. Fischer projections of various stereosequences.

temperature has little effect on this placement. The Fischer projections of the various stereosequences are shown in Fig. 3.

Methine Carbon β to SO_2

This resonance (51.4 ppm) is resolved as a doublet only. This can be attributed to r and m diad stereosequences, although the splitting is less than that for the α -sulfonyl methine carbon.

Methylene Carbon α to SO_2

This resonance is clearly split into two peaks (56.1 and 55.3 ppm) which may also be due to m and r diads. However the intensity ratio is 2,3, in disagreement with values in the range 5.0 to 5.8 observed for protons and the α -sulfonyl methine carbon in SVVS sequences. It is possible that the resonance position is equally sensitive to M and R "diad" placements with the asymmetric centre to the left (across SO_2) and that the observed splitting is actually a composite of several overlapping peaks.

Methylene Carbon β to SO_2

There was no observable splitting on this resonance (35.5 ppm), although spectra for copolymers with $n > 2$ indicated that there is probably a weak downfield peak, which is being obscured by the solvent in the present case.

Copolymers with $n > 2$

Figure 4 shows the spectrum of a copolymer with $n = 2.8$. This copolymer, as well as one with $n = 3.9$, did not give any resonances at 66.7 and 49.7 ppm, confirming the PMR result that SVS sequences

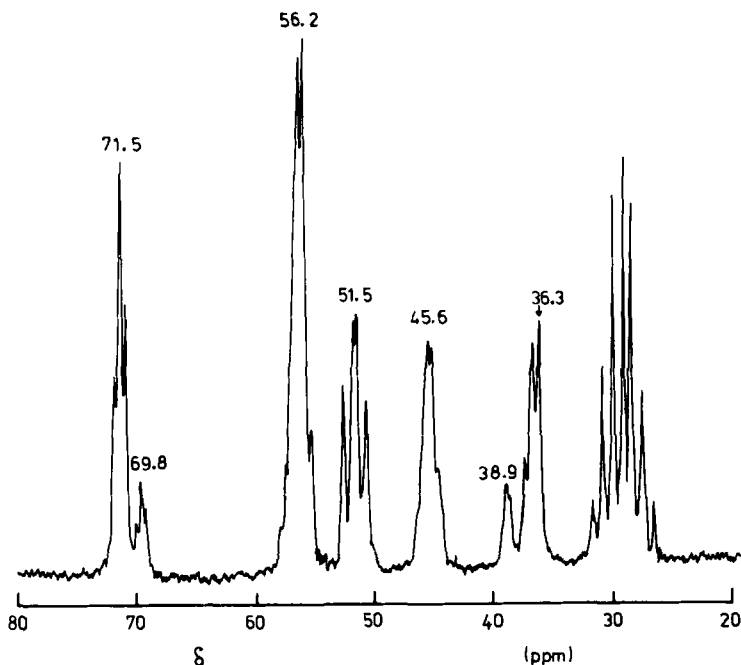
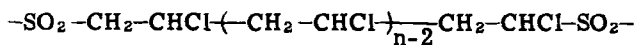


FIG. 4. Spectrum of poly(vinyl chloride sulfone) with $n = 2.8$ in acetone from 56,300 scans.

cannot be formed above 0°C . The copolymer therefore consists of $S(V)_n S$ sequences with $n \geq 2$.

By analogy with Fig. 2, it is possible to make the following assignments: α - and β -sulfonyl methine carbons at 72-69 ppm and 53-50.5 ppm and α - and β -sulfonyl methylene carbons at 56-55 and 39-36 ppm, respectively. By analogy with the reported spectrum for PVC [15], carbon atoms removed from SO_2 by more than two main-chain bonds are assigned: methine at 56.2 ppm and methylene at 45.6 ppm. These assignments are shown below:



$\delta =$ 56 52 46 56 37 70 (ppm)

This accounts for the five main peaks observed, allowing for the fortuitous chemical-shift equivalence of the α -sulfonyl methylene and PVC-type methine carbon resonances.

Figure 5 shows the spectrum for a copolymer with $n = 3.9$. The increase in n is clearly seen by comparing the spectra in Figs. 4 and 5. All peaks assigned to carbon nuclei α and β to SO_2 have decreased in intensity relative to the peaks at 56 and 46 ppm, assigned to PVC-type carbons ($\cong \gamma$ to SO_2).

The intensities of the PVC-type methylene and methine resonances should be equal, however the methine peak is more intense due to the overlap with the α -sulfonyl methylene. With the carbon atoms numbered as shown (Fig. 5), it was found for both $n = 2.8$ and $n = 3.9$ that $A_6 = A_5 = A_2$ and that $A_{(1+4)} - A_2 = A_3$ within $\pm 10\%$ supporting the assignments.

The small peak associated with resonance area 5 (38.9 ppm) is probably due to the *m* diad stereoisomer in VVS sequences, which

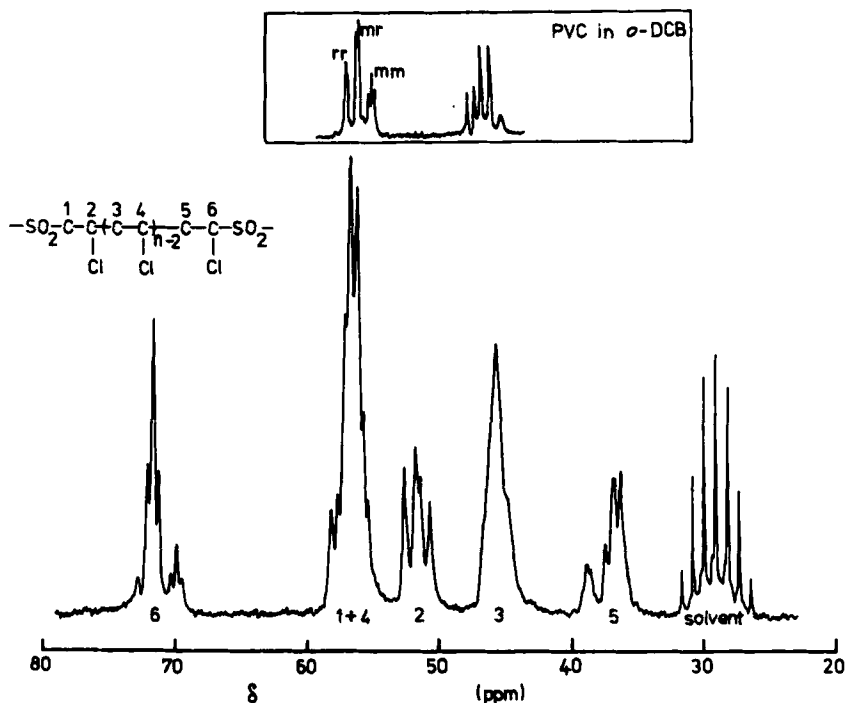


FIG. 5. Spectrum of poly(vinyl chloride sulfone) with $n = 3.9$ in acetone from 65,000 scans.

was not observed in the 2:1 copolymer due to solvent overlap. If this is the case, it shows that the β -methylene and α -methine positions in VS diads are most sensitive to VVS "internal" stereosequences. This is reasonable in view of the steric interactions that must occur in VS sequences, where the chlorine substituent is α to SO_2 .

Fine Structure

Generally, all peaks showed at least triplet fine structure, indicating the resolution of triad stereosequences. There is apparently no discrimination of $S(V)_n S$ sequences with $n = 2$ and 3 (and higher), or if there is, it is masked by the more dominant tacticity splittings (cf. PVC, Fig. 5). The smearing of peak 3 (PVC-type methylene) may be due to different sequence lengths. The greater multiplet structure on peak 1 + 4 in Fig. 5 compared with Fig. 4 may also be due to a small shift in either peak 1 or peak 4 with increased n value, reducing the overlap.

A detailed analysis of the fine structure cannot be made without a study of model compounds. Both "internal" and "across SO_2 " tacticity effects have to be considered and the spectra are further complicated by the overlap of resonances arising from different vinyl chloride sequence lengths.

CONCLUSIONS

1. The spectrum of the copolymer with $n = 1.1$ showed both methylene and methine carbons in SVS sequences to be sensitive to "diad" tacticity "across SO_2 ."

2. No SVS sequences were observed in the spectrum of the copolymer with $n = 2.0$, in accord with PMR results which showed that these sequences are negligible in this copolymer. Furthermore, the high stereoregularity of the SVVS "internal" stereosequence diad was confirmed.

3. Copolymers with $n > 2$ gave complex spectra, in which the resonances due to different chemical shifts showed multiplet splitting due to stereosequence effects. There was a fortuitous chemical-shift equivalence of the α -sulfonyl methylene and PVC-methine resonances.

4. The internal consistency of peak areas showed that there was no significant differential nuclear Overhauser enhancement.

ACKNOWLEDGEMENTS

We wish to thank the Australian Institute of Nuclear Science and Engineering (AINSE) for supporting this work, the Australian Atomic

Energy Commission (AAEC) for use of irradiation facilities, Mr. E. A. Palmer and Mr. M. Lavers (AINSE) and Mr. D. F. Sangster (AAEC) for organizational assistance, Mr. J. Bolton and Mr. J. Gray (AAEC) for irradiation of samples, and the Department of Education for a CPG studentship for R.E.C.

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Accepted by editor March 7, 1975

Received for publication September 16, 1975