

A reappraisal of the stereochemistry of polysilylenes formed by the *Wurtz* reductive-coupling reaction¹

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Abstract

The polymer chain microstructures of poly(methylphenylsilylene), poly(methyl-*p*-tolylsilylene) and poly(cyclohexylmethylsilylene) prepared by three different modifications of the alkali-metal-mediated reductive-coupling of the corresponding dichloroorganosilanes have been studied using ²⁹Si NMR spectroscopy. Deconvolution software has been used to obtain accurate integrals of the resonances associated with isotactic, syndiotactic and heterotactic triads in the spectra of the polymers. In all cases, and in contrast with the observations of previous studies, the polymer structures were observed to accord with models based on Bernoullian statistics.

Keywords: Silicon; Polysilylenes; Stereochemistry; *Wurtz* reductive-coupling; Nuclear magnetic resonance; Deconvolution

1. Introduction

Stereochemistry in polysilylenes (polysilanes) differs from that of the more familiar vinyl polymers in one very significant way. Whereas in the latter only alternate main chain atoms are stereogenic centres, in polysilylenes in which the two main chain substituents are different, they are all stereogenic centres. By definition, polymers in which the relative configurations of successive stereogenic centres are all meso (*m*) are isotactic, those in which they are all racemic (*r*) are syndiotactic and those in which they are random are atactic. These definitions applied to triads of silicon atoms in an unsymmetrically substituted polysilylene are depicted in Fig. 1 as planar zig-zag configurations. It is readily seen that the familiar association of an isotactic structure of a vinyl polymer with like substituents lying to the same side of the polymer chain does not apply to polymers in which all the chain atoms are stereogenic centres.

The determination of configuration and stereochemistry in polysilylenes has focused more on studies of the

²⁹Si NMR spectra of the polymers than of ¹H and ¹³C spectra associated with the substituents [1]. Notwithstanding the low abundance of ²⁹Si, the long relaxation time of the nucleus and its negative magnetogyric ratio, polysilylenes give rise to spectra which are abundant in configurational information. For polymers prepared by conventional *Wurtz* reductive-coupling of the corresponding dichloroorganosilane [2,3] depicted in Scheme 1, Wolff et al. [4] discussed the ²⁹Si NMR spectra of a series of polydialkylsilylenes. These included the symmetrically substituted poly(di-*n*-hexylsilylene) for which, as expected, there was only a single sharp resonance. In contrast, the unsymmetrically substituted polymers displayed broad symmetrical five- to seven-line patterns centred at chemical shifts lying between –20 and –32 ppm, which were interpreted as arising from incompletely resolved spectra of the central atoms of the pentad sequences in atactic polymers. Included in the series was poly(cyclohexylmethylsilylene) (PHMS), for which only a single broad resonance was observed, and this was attributed to unresolved splitting.

Wolff et al. [5] also report the ²⁹Si NMR spectra of poly(methylphenylsilylene) (PMPS) and of copolymers of this unit and selected dialkylsilylene units. Of particular relevance to the present work is the interpretation of the spectrum of PMPS, which consists of three overlapping resonances at –39.2, –39.9 and –41.2

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ppm with relative intensities of 0.30:0.30:0.40 ($\pm 5\%$). The authors reasoned that these should be assigned to syndiotactic, isotactic and heterotactic triads respectively. Further splitting within the spectrum can be observed as shoulders or minor peaks on the sides of these resonances, but the extended interactions observed in the unsymmetrical polydialkylsilylenes are less obvious for this polymer. It was noted that the intensity ratio for the three resonances was not that expected for an atactic polymer (1:1:2), and from this it was inferred that the polymer was partially tactic. Furthermore, notwithstanding the fact that these preferred assignments and intensity ratios do not accord with Bernoullian statistics, when such a model was applied to an assignment of the resonances in which the most intense peak was considered to correspond to either isotactic or syndiotactic rather than heterotactic triads, these alternative assignments were discounted. Thus, during the normal *Wurtz* formation of PMPS it could be concluded that tacticity is dependent upon more than a single probability factor. Based on arguments concerned with 1,3 interactions affecting the stereochemistry of silane addition, i.e. the stereochemistry of the silylene β to the adding silane unit giving the new one a tendency to add with like stereochemistry, they calculated that only a 60% abundance of such stereogenically equivalent units at 1,3 positions would be enough to produce the observed 3:3:4 relative intensities.

Recently, calculations based on the probability of retention of configuration, or otherwise, at the atoms involved in the addition reaction in the ring opening polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclo-tetrasilanes, Fossum and Matyjaszewski [6,7] re-assigned the three resonances in the ^{29}Si NMR spectrum of PMPS as heterotactic (-39.2 ppm), syndiotactic (-39.9 ppm) and isotactic (-41.2 ppm). Since configurations were determined by the structures of the cyclic precursors to these polymers, Bernoullian statistical analysis of their tacticity was not relevant.

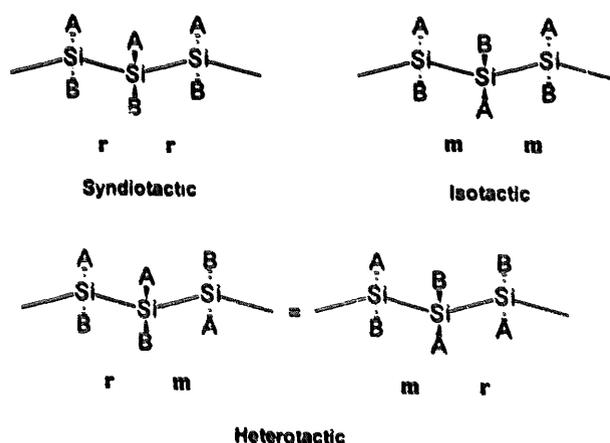
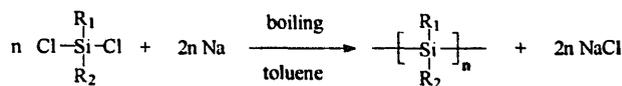


Fig. 1. Triad sequence distributions in an unsymmetrical polysilylene.



Scheme 1.

In this paper we present a reappraisal of the chain microstructures of three polysilylenes with bulky substituents that have been prepared using various *Wurtz* methodologies. These are PMPS, poly(methyl-*p*-tolylsilylene) (PMTS), and PHMS. The analysis is based on the deconvoluted ^{29}Si NMR spectra of the polymers and a consideration of the stereochemistry of silane addition in terms of a simple Bernoullian statistical model. The nature of the substituents are seen to have a significant effect, both in terms of the assignments of the NMR resonances to triad configurations and in the determination of these configurations during the course of the polymerization.

2. Experimental

Polysilylenes were prepared by three modifications of the *Wurtz* reductive-coupling of the corresponding dichloroorganosilanes, details of which are recorded elsewhere. In summary they are as follows: (i) the standard methodology in which the dichlorosilane is added to a slight stoichiometric excess of molten sodium dispersed in boiling toluene [1,2]; (ii) a lower temperature modification in which the dichlorosilane is added to a slight stoichiometric excess of a sodium sand dispersed in boiling diethyl ether containing 15-crown-5 [8,9]; (iii) a method whereby the dichlorosilane is added to a small excess of C_8K (formed by heating potassium in purified graphite) in THF at temperatures between -79 and -15°C [10,11]. Reactions were carefully quenched in methanol in a procedure which is also designed to consume any remaining alkali metal. Polymers were extracted using hexane to remove oligomeric material and were then redissolved in THF before reprecipitation in methanol. Solvents were dried by standard procedures and dichlorosilane reagents were handled using Schlenk line methods. Other details common to all three methods, including the suppliers of reagents, have been reported previously [8]. Polymers were identified as polysilylenes by ^1H and ^{13}C NMR spectroscopy, as well as by ^{29}Si NMR spectroscopy which is central to this study. The ^{29}Si spectra were recorded at 53.34 MHz using inverse gated decoupling to acquire the silicon spectra without NOE and give quantitative results. Spectra were recorded at probe temperature using a Jeol GX-270 spectrometer from solutions in CDCl_3 using $\text{Cr}(\text{acac})_3$ as a spin relaxation agent. Chemical shifts were referenced to the absolute fre-

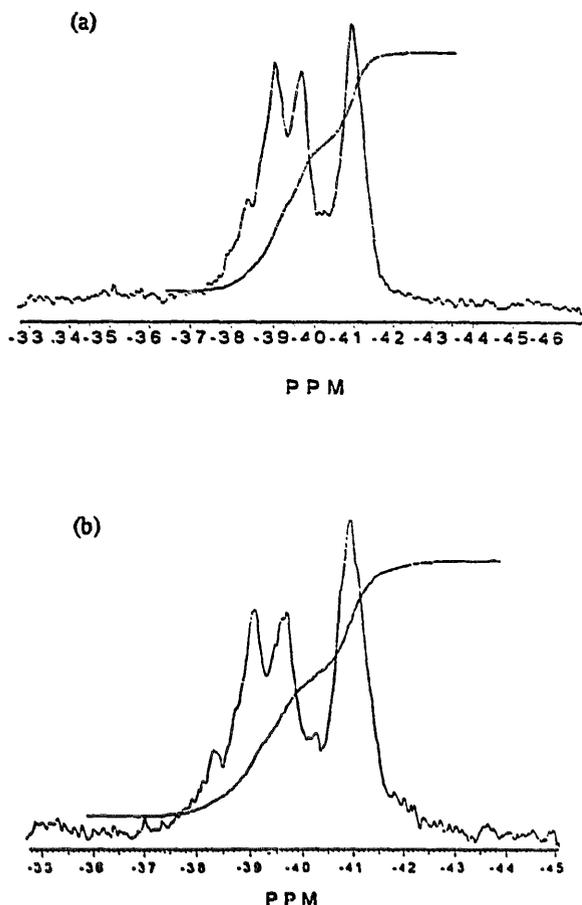


Fig. 2. 53.54 MHz ^{29}Si NMR spectra of PMPS isolated from (a) a standard *Wurtz* reductive-coupling reaction using sodium in boiling diethyl ether, and (b) the graphite phase of a C_8K -mediated reductive-coupling of dichloromethylphenylsilane in THF.

quency of TMS. Peak deconvolutions were achieved using PeaksolveTM, a peak fitting package for WindowsTM supplied by Galactic Industries Corporation.

3. Results and discussion

Two ^{29}Si NMR spectra of PMPS that we have previously reported [10] are reproduced in Fig. 2. The first of these is for a polymer produced using the *Wurtz* reductive-coupling reaction in boiling diethyl ether, whilst the second is for a polymer produced using the graphite intercalate, C_8K , as the reducing agent in THF solution at -79°C . Although the first of these polymers was not prepared by the exact *Wurtz* methodology employed by Wolff et al. [5], its spectrum is in all respects identical to that obtained by them, and the 0.30:0.30:0.40 ($\pm 5\%$) intensity ratio that they observed is evident from the spectrum integral. The second spectrum shows a relative enhancement of the high field resonance at the

expense of the other two. For this polymer the intensity ratio based on simple integration is very close to 1:1:2, and if the assignments of Wolff et al. are accepted this would not only accord with Bernoullian statistics but the polymer would appear to be completely atactic. However, the arguments of Fossum and Matyjaszewski [6,7] are quite compelling, and if their assignments of the resonances are accepted then this polymer is significantly more isotactic than the first. It should also be noted that on this basis, for neither polymer is there an accordance of configuration with Bernoullian statistics. Bernoullian statistics applied to triad configurations in polymers with stereogenic centres require that a single probability factor determines successive placements. This is usually taken to be the probability of a meso placement p_m and the probability of a racemic placement p_r is then simply $1 - p_m$, and the relative proportions of heterotactic, syndiotactic and isotactic triads are given by the probabilities of two successive placements, thus:

$$P_H : P_S : P_I = 2p_m(1 - p_m) : (1 - p_m)^2 : p_m^2$$

Based on the intensity of the highest field resonance, p_m is 0.63 for the polymer of Fig. 2(a) and the calculated intensity ratio would be 0.46:0.14:0.40, whilst for the polymer of Fig. 2(b) p_m would be 0.71, giving an intensity ratio 0.41:0.09:0.50. In either case it would be concluded that a Bernoullian statistical model does not apply.

These same two spectra when deconvoluted reveal triad proportions very different from those taken directly from the integrals of the three resonances. Fig. 3 shows the spectra, the three deconvolution components and their resultants. The agreement of the resultants with the actual spectra is very good. Deviations are evident on the low field side of the first peak and between the second and the third peaks but these are to be expected, since in both regions fine structure associated with higher order sequences is evident². The only other region at which the correspondence is less than perfect is at the tops of the low field peaks, where small fractions of the integrals seem to have been excluded and added to the integrals at the minima between the first and second peaks. These areas represent less than 1% of the low field peak integrals and no more than 0.5% of the total integrals for both spectra.

Reading from low field to high field then the intensity ratios for Figs. 3(a) and 3(b) are 0.48:0.15:0.37 and 0.44:0.12:0.44 respectively. For the purposes of comparison Table 1 lists these ratios alongside those

² Deconvolutions to accord with the ten possible pentad sequences were investigated but the correlations were poor in comparison with those found for triad sequences.

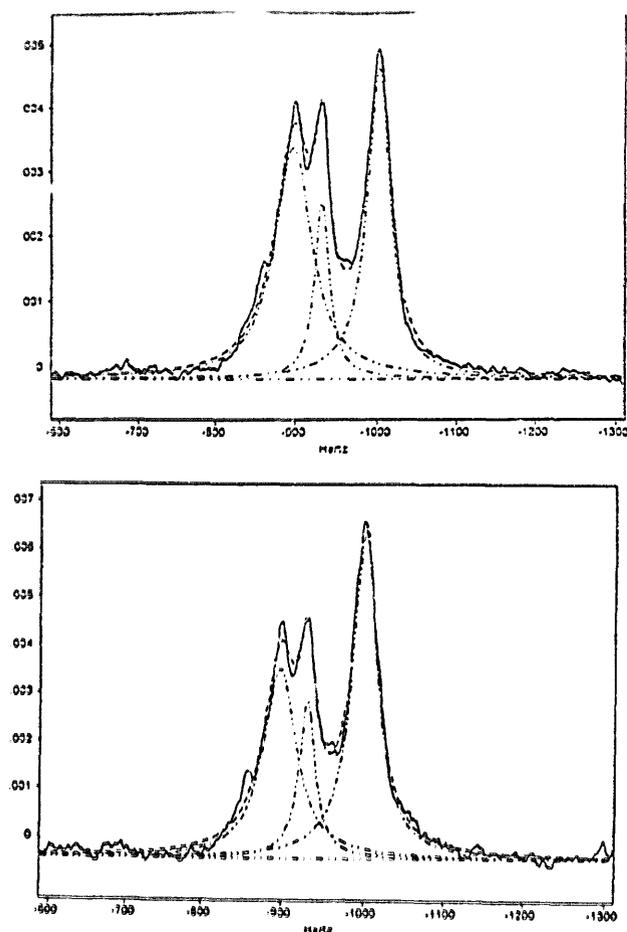


Fig. 3. Deconvolutions of the NMR spectra of Fig. 2: —, spectrum; ---, deconvoluted peaks; ···, spectrum fit.

that would be calculated from the intensity of the high field peak for the assignments of (i) Wolff et al. [5], and (ii) Fossum and Matyjaszewski [6,7], assuming in each case that Bernoullian statistics apply. The data from Fig. 3(b) are not particularly informative, as under either assignment the same value of p_m arises. The conclusion is therefore ambiguous, in that the high field peak could correspond to either heterotactic or isotactic triads. However, the best agreement for the data taken from Fig. 2(a) is found for the assignments of Fossum and

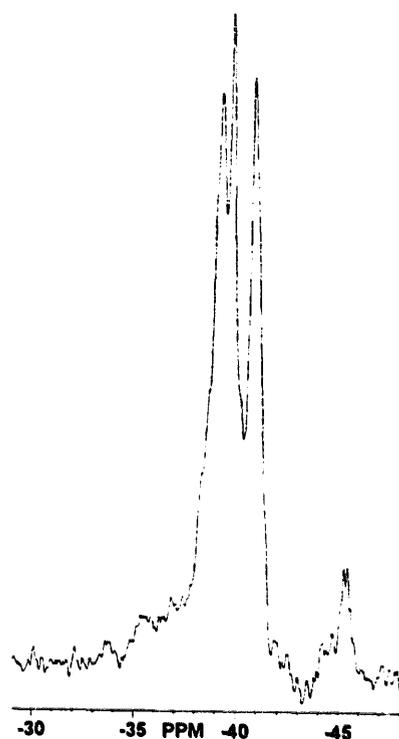


Fig. 4. 53.54 MHz ^{29}Si NMR spectra of PMTS isolated from a standard Wurtz reductive-coupling reaction.

Matyjaszewski and the agreement is so good that it can be taken as evidence in support of their assignments. Furthermore, accepting their assignments, though it is still clear that the effect of using the potassium-graphite intercalate C_8K as the reducing agent in the reductive-coupling of dichloromethylphenylsilane leads to a polymer of higher isotactic content than that from the Wurtz reaction as it is usually carried out, it must be noted that the isotactic contents of both polymers are less than originally reported whilst the heterotactic content is significantly higher [5,10].

Fig. 4 depicts the ^{29}Si NMR spectrum of PMTS. This polymer has only been prepared using the conventional Wurtz methodology, as the C_8K method results in a product that is thought to include phenyl groups in the main chain. Thus, no comparison of tacticity from the

Table 1

Bernoullian statistics applied to different peak assignments of the triad configurations of PMPS and PMTS taken from the deconvoluted ^{29}Si NMR spectra of Figs. 3 and 4

Assignment	Fig. 3(a) PMPS			Fig. 3(b) PMPS			Fig. 4 PMTS			
		p_m	Expt.	Calc.	p_m	Expt.	Calc.	p_m	Expt.	Calc.
Wolff et al.	I	0.69	0.48	0.48	0.66	0.44	0.44	0.60	0.36	0.36
	S		0.15	0.09		0.12	0.12		0.17	0.16
	H		0.37	0.43		0.44	0.44		0.47	0.48
Fossum and Matyjaszewski	H	0.61	0.48	0.48	0.66	0.44	0.44	0.69	0.36	0.43
	S		0.15	0.15		0.12	0.12		0.17	0.10
	I		0.37	0.37		0.44	0.44		0.47	0.47



Scheme 2.

use of the different modifications of the reaction is possible. These resonances have never previously been assigned, but since the spectrum appears in exactly the same region as that of PMPS, between -38 and -42 ppm³, and in all other respects is very similar, it was assumed that the assignments of the triad configurations would be exactly the same as those for PMPS. However, quite surprisingly, the analysis in accordance with a Bernoullian statistical model shows a more satisfactory correlation with the triad assignments of Wolff et al. than with those of Fossum and Matyjaszewski. It is hard to rationalize this observation, for although substitution at the para position of the phenyl ring might be expected to influence the probabilities of successive placements during the polymer forming reaction, there is no apparent reason why it should have such a simple yet profound effect on the chemical shifts of the heterotactic and isotactic triad environments. It could be argued that in this case the polymerization does not accord with a Bernoullian statistical model, and that in determining the polymer tacticity there is more than one probability influencing successive main chain configurations during the addition reaction. However, such a minor structural change at points remote from the centre of reaction would not be expected to have such a significant effect on a reaction that is now generally accepted [8,12,13] to be an S_N2 attack of a silyl anion on a dichloroorganosilane molecule as depicted in Scheme 2.

Since the variation of the probability of heterotactic triads is symmetrical about $p_m = 0.5$, the Bernoullian model allows for the interchange of the probabilities of meso and racemic placements. Therefore, it should be pointed out that in the absence of any further independent evidence concerning the assignments of the three

³ The polymer was of quite low molecular weight and the resonance at about -45 ppm is attributed to silicon atoms in the position β to end groups.

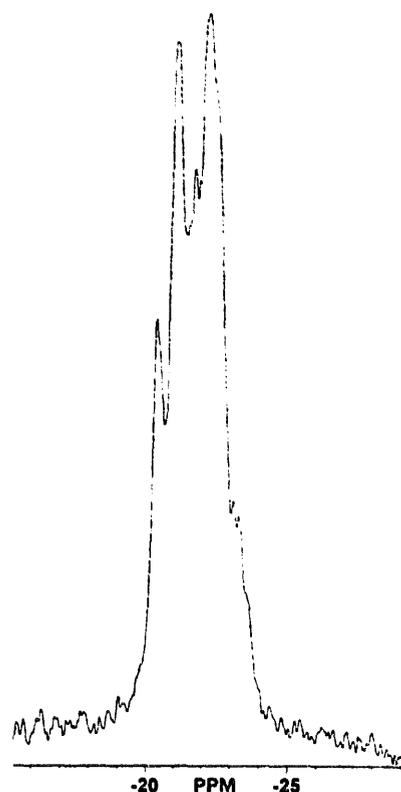


Fig. 5. 53.54 MHz ^{29}Si NMR spectra of PHMS isolated from a standard Wurtz reductive-coupling reaction.

resonances in the spectrum of PMTS, although they are in apparent accordance with those of Wolff et al. for PMPS, they would still accord with Bernoullian statistics if the assignments of the isotactic and syndiotactic peaks were interchanged. There is no basis for doing this, but the possibility must not be discounted.

In sharp contrast is the spectrum of a sample of PHMS prepared in accordance with the conventional Wurtz methodology, which is depicted in Fig. 5. Three principal resonances are again evident, but relative to the spectra of the alkyl/aryl-substituted polysilylenes they have moved by about 20 ppm to the range -19 to -23 ppm. Furthermore, on the basis of the above statistical arguments, even simple inspection seems to indicate the assignment of the outer peaks as isotactic and syndiotactic. In essence, this assigns the central resonance unambiguously to heterotactic triads. Again

Table 2

Bernoullian statistics applied to peak assignments of the triad configurations of samples of PHMS taken from their deconvoluted ^{29}Si NMR spectra

Assignment	Wurtz method			C ₈ K method		
	p_m	Expt.	Calc.	p_m	Expt.	Calc.
I (or S)	0.82	0.65	0.67	0.71	0.50	0.50
H	or	0.27	0.29	or	0.41	0.41
S (or I)	0.18	0.08	0.04	0.29	0.09	0.09

assuming that a Bernoullian statistical model applies, Table 2 allows comparison of the experimentally determined and calculated values of the intensity ratios for the three triads based on these assignments, both for the spectrum of Fig. 5 and for the spectrum of a sample of PHMS prepared using the C_8K modification. In the latter case the agreement with the Bernoullian model is excellent. In the former the fit is not quite so good, but the error in the experimental determination of the smallest of the probabilities is quite high in this case. It should be noted that the interchange of the assignment of the heterotactic triad with either of the other possibilities leads to ridiculous results. On the Bernoullian model, heterotactic triads cannot be present in more than 50% abundance, so they cannot correspond to the one presently assigned as I (or S) for the polymer prepared using the conventional Wurtz reaction. Similarly, if the peak of lowest intensity is reassigned as corresponding to the heterotactic triad, either p_m or p_r , would have to be as high as 0.95, which on the Bernoullian model would require this polymer to be almost completely isotactic or completely syndiotactic, which it clearly is not.

Though the effects of preparative methods are not the subject of this paper, it is worth noting that the use of C_8K as the reductive-coupling agent in the polymerization reaction has again resulted in a significant change in tacticity of the polymer. Whereas for PMPS it could be stated with some assurance that the C_8K method gives a polymer which is more isotactic, at this stage it is only possible to say that for PHMS, the effect is to make it more atactic. Whether this is from a starting point of greater isotacticity or greater syndiotacticity is impossible to say.

In conclusion, though it has not proved possible to unequivocally assign the three dominant resonances in the ^{29}Si NMR spectra of PMPS, PMTS and PHMS, it has nonetheless been shown that they accord with Bernoullian statistical models for the chosen modifications of the Wurtz polymerization reactions that lead to their formation. The three polymers of this study were selected for their bulky substituents, and from the results it is clear that these play a part in determining the isotactic, heterotactic and syndiotactic triad configurations of the resultant polymers. Most probably it is the interaction of the substituents with the alkali metal

surface or the lamellae of the graphite intercalate during addition reactions that determines the stereochemistry of a specific polymer. Such effects were not apparent for the unsymmetrical poly(methyl-*n*-alkylsilylene)s studied by Wolff et al., so it would be of interest to apply deconvolution software to ^{29}Si NMR spectra in a similar study of these polymers to check that a Bernoullian model applies and to confirm that NMR peak distributions conform to those expected for atactic polymers.

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