JOURNAL OF MATERIALS SCIENCE 30 (1995) 5371–5380

Synthesis of silicon oxynitride from a polymeric precursor

Part IV *Pyrolysis of the copolymers*

GA-ER YU°*, MOHAN EDIRISINGHE*§, D. FINCH*, B. RALPH*, J. PARRICK°
*°Departments of Chemistry and *Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

In this final part of our investigation, the copolymers prepared (reported in Part III) have been pyrolysed to yield silicon oxynitride. Thermogravimetric studies performed on several copolymers in nitrogen, ammonia/nitrogen mixtures, air and oxygen are discussed in the present paper. One copolymer was used for further investigation and its pyrolysis conditions (variation of pyrolysis atmosphere according to temperature) were optimized to produce the maximum yield of white amorphous residue which was crystallized by heating to 1600 °C to produce silicon oxynitride powder. The powder particles were equiaxed in shape and in the size range 50–150 nm but in agglomerates of size 0.3–0.1 μm. Crystallization at higher temperatures resulted in a mixture of α silicon nitride–silicon oxynitride.

1. Introduction

The synthesis of the ceramic silicon oxynitride from polymeric precursors consists of several stages. The precursor is a copolymer obtained by reacting together methylcyclosiloxanes and methylcyclosilazanes. In Part I we described the preparation of methylcyclosiloxanes, containing > 95 mol % of cyclic tetramer, pentamer and hexamer, by hydrolysing dichloromethylsilane [1]. The preparation of trimethylcyclotrisilazane and tetramethylcyclotetrasilazane by ammonolysis of dichloromethylsilane in diethyl ether or tetrahydrofuran (THF) under well-defined, reproducible conditions with adequate process control was described in Part II [2]. In Part III the copolymerization of the methylcyclosiloxanes and methylcyclosilazanes was carried out under different experimental conditions to produce several copolymers and their structural details were predicted with the aid of results from homopolymerization experiments on the methylcyclosiloxanes and the methylcyclosilazanes [3]. In this final part, the pyrolysis of these copolymers is investigated using thermogravimetric analysis. One copolymer is investigated further to optimize the pyrolysis atmosphere according to temperature to produce a white amorphous residue which, on crystallization under suitable conditions, produces a silicon oxynitride (Si_2ON_2) powder with submicrometre size particles.

It is well-known that the pyrolysis atmosphere and temperature are major processing variables in synthesizing nitrogen ceramics from polymeric precursors. The pioneering work of Seyferth and co-workers [4] showed that preceramic polymers prepared using mixtures of dichlorosilane and methyldichlorosilane produced a higher yield of silicon nitride when pyrolyzed in a reactive atmosphere such as ammonia compared with pyrolysis in nitrogen or argon when other carbon-containing compounds were also produced. Blum and co-workers [5] give detailed chemical analyses of several ceramics synthesized from polymeric precursors and their results indicate clearly that pyrolysis in ammonia, compared with nitrogen, reduced the carbon content in the product by an order of magnitude. Yu and Mah [6] reported the synthesis of silicon oxynitride from a "living" polymer (produced using polysiloxanes and polysilazanes but no further details were given) which was pyrolysed in ammonia at 1000 °C. However, pyrolysis of this polymer in nitrogen or argon produced a mixture of silicon nitride and silicon carbide [4]. Burns and Chandra [7] have shown that several cross-linked polycarbosilanes, polysilanes and polysilazanes can be pyrolysed in nitrogen or ammonia at 1200 °C to produce amorphous silicon nitride. Recently, Funayama and co-workers [8] pyrolysed a polyborosilane in ammonia and crystallized the resulting product in nitrogen to synthesize a mixture of α and β silicon nitride (Si_3N_4). However, the question as to whether a single polymeric precursor is able to produce several types of ceramics if pyrolysed, and subsequently crystallized, under different conditions is not addressed specifically in the literature.

In the present work we also show that the same copolymer produces amorphous residues of different nitrogen ceramics when the pyrolysis atmosphere is varied according to temperature. Thus, by introducing

---

[§] Author to whom all correspondence regarding Parts I–IV should be sent.

0022–2461

ammonia to the pyrolysis chamber, in the temperature range 500–700 °C, instead of nitrogen, which was used as the pyrolysis atmosphere at all other temperatures, an amorphous residue of Si_2ON_2 rather than αSi_3N_4 was obtained. The amorphous Si_2ON_2 residue can be crystallized at different temperatures to produce Si_2ON_2 powder or αSi_3N_4–Si_2ON_2 mixtures.

2. Experimental procedure

2.1. Copolymer

The methods of preparation of the copolymers were discussed in Part III [3]. Copolymers P4, P5, P6, P11A and P11B were used in the present work. The copolymerization conditions used in their preparation are given in Table I. THF was used as the solvent. KH powder and CH_3I or $(CH_3)_3SiCl$ were used for initiation and termination of the polymerization reaction, respectively. The copolymers (white solids) were produced with a yield of > 95 wt %.

2.2. Thermogravimetry

A Perkin-Elmer TG2 instrument was used. The glass tube of the instrument was modified so that thermal decomposition of the copolymers could be investigated in nitrogen and in an ammonia/nitrogen mixture (about 2:1 by volume). Ammonia gas was dried by passing through successive columns containing barium oxide particles and sodium on glass wool. Some experiments were also carried out in air and oxygen atmospheres. Air was supplied by an air pump. Each copolymer was pyrolysed from 40 °C to approximately 980 °C with a temperature ramp of 10 °C min^{-1} and in each case the gas flow rate was approximately 80 ml min^{-1}. Previous work [9] has shown that the thermogravimetric curves of the copolymers used in the present work are not affected significantly by the heating rate.

2.3. Pyrolysis (tube furnace)

The copolymer was placed in an alumina holder and pyrolysed in a tube furnace in the presence of flowing nitrogen or ammonia (flow rate 80 ml min^{-1}) and dried by a method similar to that mentioned in section 2.2. The furnace tube was at 120 °C when the copolymer was inserted and heating to 1000 °C was carried out at 100 °C h^{-1} followed by soaking at this temperature for 2 h. Subsequently, the furnace was switched off and allowed to cool to room temperature.

2.4. Crystallization

The residue after pyrolysis was ground to a fine powder using a mortar and pestle and pressed into the shape of a small disc. It was encapsulated in a commercially available silicon oxynitride powder (a mixture of α and β Si_3N_4 and Si_2ON_2 as detected by X-ray diffraction) and further pressed to produce a thicker disc. This encapsulation prevented the pyrolytic residue from reacting with any oxygen and moisture present in the nitrogen during heat treatment. The disc was heated in the tube furnace used for pyrolysis in the presence of flowing nitrogen (flow rate 80 ml min^{-1}) from 150 to 1600 °C at 60 °C h^{-1}, soaked at this temperature for 2 h and subsequently cooled to room temperature at 60 °C h^{-1}. Some samples of the pyrolysed product (in disc form as above) were heated similarly but according to a different temperature cycle where heating from 150 to 800 °C and subsequently to 1660 °C was carried out at 2 °C min^{-1} and 1 °C min^{-1}, respectively. These samples were soaked at 1660 °C for 5 h before cooling to 850 °C at 1 °C min^{-1} and then to room temperature in the furnace.

2.5. Fourier transform infra-red (FT–IR) spectroscopy

The pyrolytic residues and the crystallized ceramic powder were investigated using a Nicplan FT–IR microscope to obtain the FT–IR spectra in the range 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were corrected automatically for variations of the baseline.

2.6. X-ray and microscopical characterization

The crystallized ceramic powder was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray studies were done using a Philips X-ray diffractometer (CuK_α radiation of wavelength 0.15418 nm and a Ni filter) operating at 35 kV and 20 mA. The scan range was 5 to 90° accompanied by a step size of 0.05° and a scan speed of

TABLE I Copolymerization conditions and details of resulting copolymers. MCSX and MCSZ denotes methylcyclosiloxanes and methylcyclosilazanes, respectively

	P4	P5	P6	P11A	P11B
Mass of MCSXs (g)	1.0	2.0	0.6	0.6	0.6
Mass of MCSZs (g)	1.2	2.0	1.2	1.0	1.0
Molar ratio of N:O in the reactants	1.2:1	1:1	2:1	2:1	2:1
Volume of THF (ml)	20	65	40	90	90
Mass of KH (g)	0.06	0.05	0.05	0.05	0.05
Reaction temperature (°C)	20	20	20	60	60
Reaction time (h)	24	24	20	10	24
Volume of CH_3I or $(CH_3)_3SiCl$ used	2.0[a]	2.0[a]	2.0[a]	–	0.2[b]

[a] CH_3I.
[b] $(CH_3)_3SiCl$.

TABLE II Summary of results of TGA experiments

Copolymer	Atmosphere	First weight loss		Second weight loss		Final residual weight (% at 980 °C)	Colour of residue
		Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)		
P4	N_2	178–400	7.8	580–890	9.1	78.8	black
	NH_3/N_2	150–397	10.4	568–840	11.0	71.8	grey
	air	189–366	6.7	459–704	10.9	80.7	black
P5	N_2	166–417	10.1	580–904	8.5	77.6	black
	NH_3/N_2	140–400	13.2	500–860	11.5	73.1	grey
	air	178–355	7.6	447–703	9.1	81.8	black
	O_2	162–340	6.5	421–658	8.1	82.8	grey
P6	N_2	161–400	9.6	577–880	8.8	77.0	black
	NH_3/N_2	133–400	13.3	574–861	10.3	72.2	grey/white
	air	189–355	7.3	447–710	9.2	82.2	black
	O_2	201–379	6.2	431–648	11.1	82.2	grey
P11A	N_2	100–440	3.6	440–980	12.3	85.0	black
P11B	N_2	120–458	20.6	529–900	8.6	69.7	black
	NH_3/N_2	120–488	24.3	554–813	8.5	66.5	grey/white

0.1° s^{-1}. SEM samples were coated with gold before examination to avoid charging effects.

3. Results and discussion

3.1. Thermogravimetry

A summary of results of the thermogravimetric studies is given in Table II. Thermogravimetric traces obtained for copolymers P4, P5, P6 and P11B are grouped according to the atmosphere in which pyrolysis took place and discussed below.

Weight loss in nitrogen takes place in two main temperature bands (Fig. 1). The first, between 150 and 450 °C corresponds to the evolution of ammonia [9] and the second, between 450 and 850 °C is due to the release of hydrocarbons [9].

The thermogravimetric curves of these four copolymers in nitrogen are similar except that different wt % of residue were obtained (Fig. 1 and Table II). Chemical analysis of the copolymers was not carried out in our investigations but the most likely reason for the different amounts of residue is the nitrogen content of each copolymer. A high nitrogen content in the copolymer can result in a low wt % of residue due to the loss of more ammonia during the first stage of pyrolysis, as indicated above.

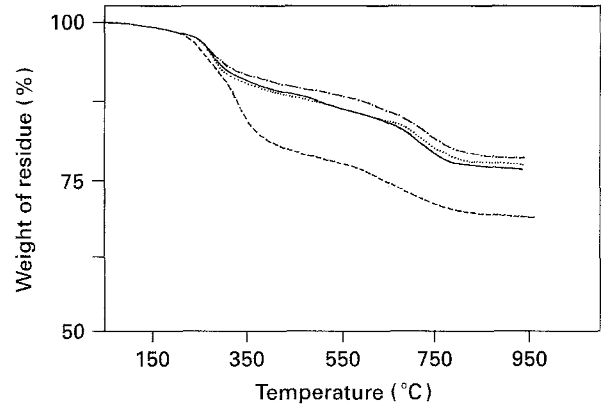


Figure 1 Thermogravimetric traces resulting from the pyrolysis of copolymers P4 (–·–·–), P5 (·····), P6 (——) and P11B (– – – –) in flowing nitrogen.

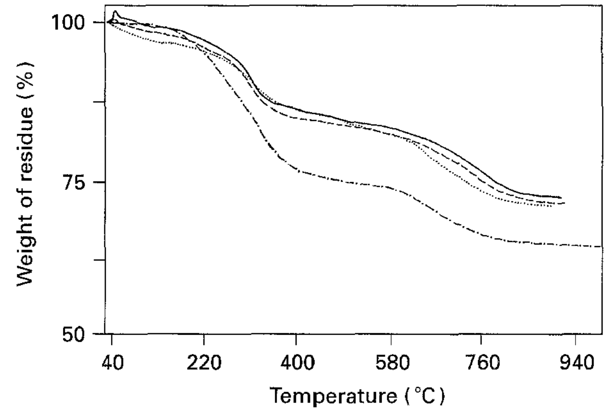


Figure 2 Thermogravimetric traces resulting from the pyrolysis of copolymers P4 (·····), P5 (——), P6 (– – – – –) and P11B (–·–·–), in a flowing ammonia/nitrogen mixture.

The thermogravimetric curves of these four copolymers in an ammonia/nitrogen mixed atmosphere (Fig. 2) are similar to those obtained in nitrogen with the major loss of weight taking place in two distinct temperature ranges which are almost identical to those for nitrogen. However, weight losses are higher than those observed in nitrogen except in one instance (Table II). Some thermogravimetric curves obtained in the ammonia/nitrogen mixed atmosphere show a small increase in weight at the beginning probably caused by the sample absorbing some ammonia.

In comparison with the other copolymers, copolymer P11B gives a significantly lower wt % of residue in nitrogen and the nitrogen/ammonia mixed atmosphere (Table II). It is interesting to compare the details of preparation of this copolymer with the others (Table I). Comparison with copolymer P11A, where all other conditions except the reaction time and the use of a reagent to terminate the polymerization reaction were identical, shows that pyrolysis in nitrogen resulted in a decrease of about 15 wt % of residue. Comparison with the other copolymers (Table I) shows that the reaction time was 20–24 h but in the case of copolymer P11B a different reagent was used to terminate the polymerization reaction and the residue after pyrolysis of P11B is 6–8 wt % lower. Therefore, it is likely that the reagent used to terminate the polymerization reaction is important in modifying the chemical structure of the copolymer formed and this has a significant influence on the weight of residue, and thereby the subsequent yield of ceramic.

Further evidence for the influence of the reagent used to terminate the polymerization reaction on the pyrolysis behaviour is contained in the thermogravimetric trace of copolymer P11A (Fig. 3). The curve shows only one major weight loss which occurs after heating to above 450 °C. This indicates that the release of ammonia (between 150 and 450 °C in the other copolymers) from P11A was more difficult. A possible reason for this could be that strong basic end groups ($N-K^+$ or $Si-K^+$), which are present in the copolymer due to the lack of a reaction to terminate polymerization, help to form a crosslinking bridge by attacking N–H or Si–H in the copolymer, thus retaining its nitrogen.

The thermogravimetric curves of copolymers P4, P5 and P6 in air (Fig. 4) show two major losses which correspond to 200–350 °C and 480–700 °C. In comparison with their thermogravimetric behaviour in nitrogen, the first weight loss in air is smaller for all three copolymers (Table II). The thermogravimetric traces in air also show an increase in wt % at about 400 °C. This is most likely to be caused by the replacement of nitrogen in the copolymer by oxygen.

The decomposition of copolymers 5 and 6 in oxygen (Fig. 5) show marked differences to those pyrolysed in air (Fig. 4). Two major weight losses are present (Fig. 5) but the rate of weight loss is much higher in oxygen indicating a faster rate of reaction.

In general, the weights of residue in both air and oxygen are higher in comparison with those in nitrogen and the ammonia/nitrogen mixture. The thermogravimetric traces of copolymer P6 in nitrogen, ammonia and air (Fig. 6) gives a direct comparison of the pyrolysis process and indicates useful trends. The residual weight after pyrolysis (w) is in the order of $w_{\text{air}} > w_{\text{nitrogen}} > w_{\text{ammonia/nitrogen}}$. The temperature at which the first weight loss begins (T_1) is in the order $(T_1)_{\text{air}} > (T_1)_{\text{nitrogen}} > (T_1)_{\text{ammonia/nitrogen}}$ and this is possibly due to the fact that oxygen helps the formation of cross-links in the copolymer at the outset so that decomposition is delayed to about 220 °C.

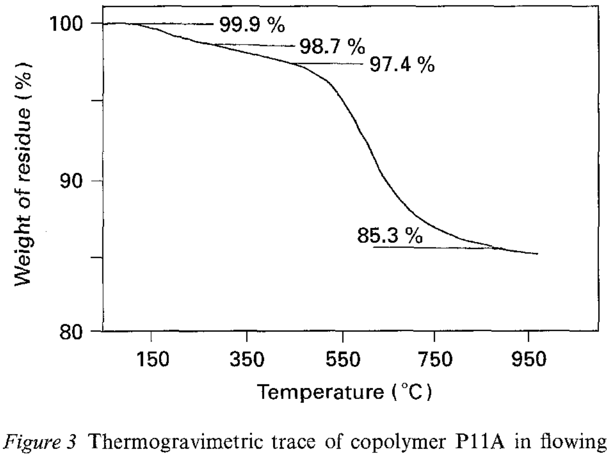


Figure 3 Thermogravimetric trace of copolymer P11A in flowing nitrogen.

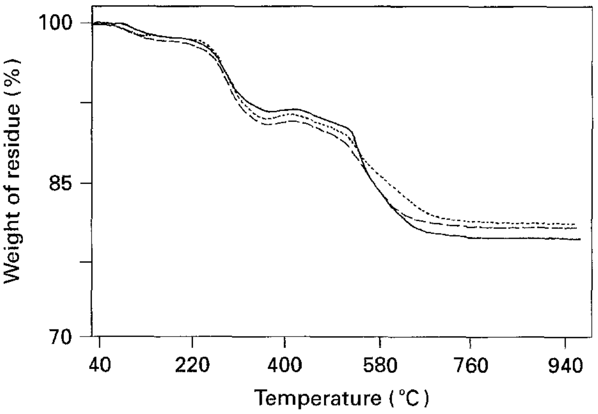


Figure 4 Thermogravimetric traces resulting from the pyrolysis of copolymers P4 (——), P5 (– – – –) and P6 (- - - - -), in flowing air.

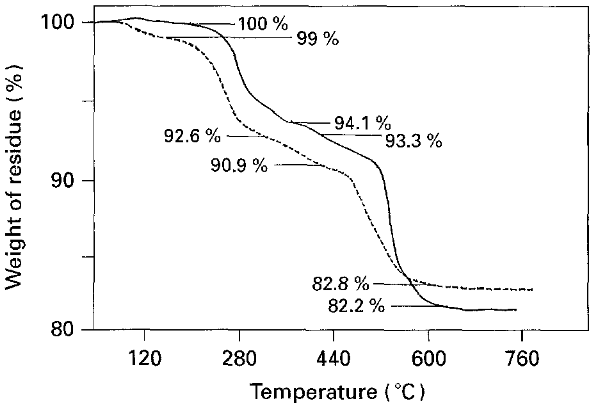


Figure 5 Thermogravimetric traces resulting from the pyrolysis of copolymers P5 (– – – –) and P6 (——) in flowing oxygen.

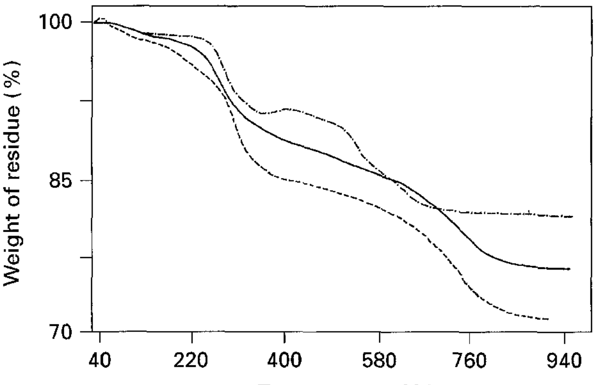


Figure 6 Thermogravimetric traces resulting from the pyrolysis of copolymer P6 in nitrogen (——) in the ammonia/nitrogen mixture (– – – –) and air (–·–·–). All three gases were flowing at 80 ml min^{-1}.

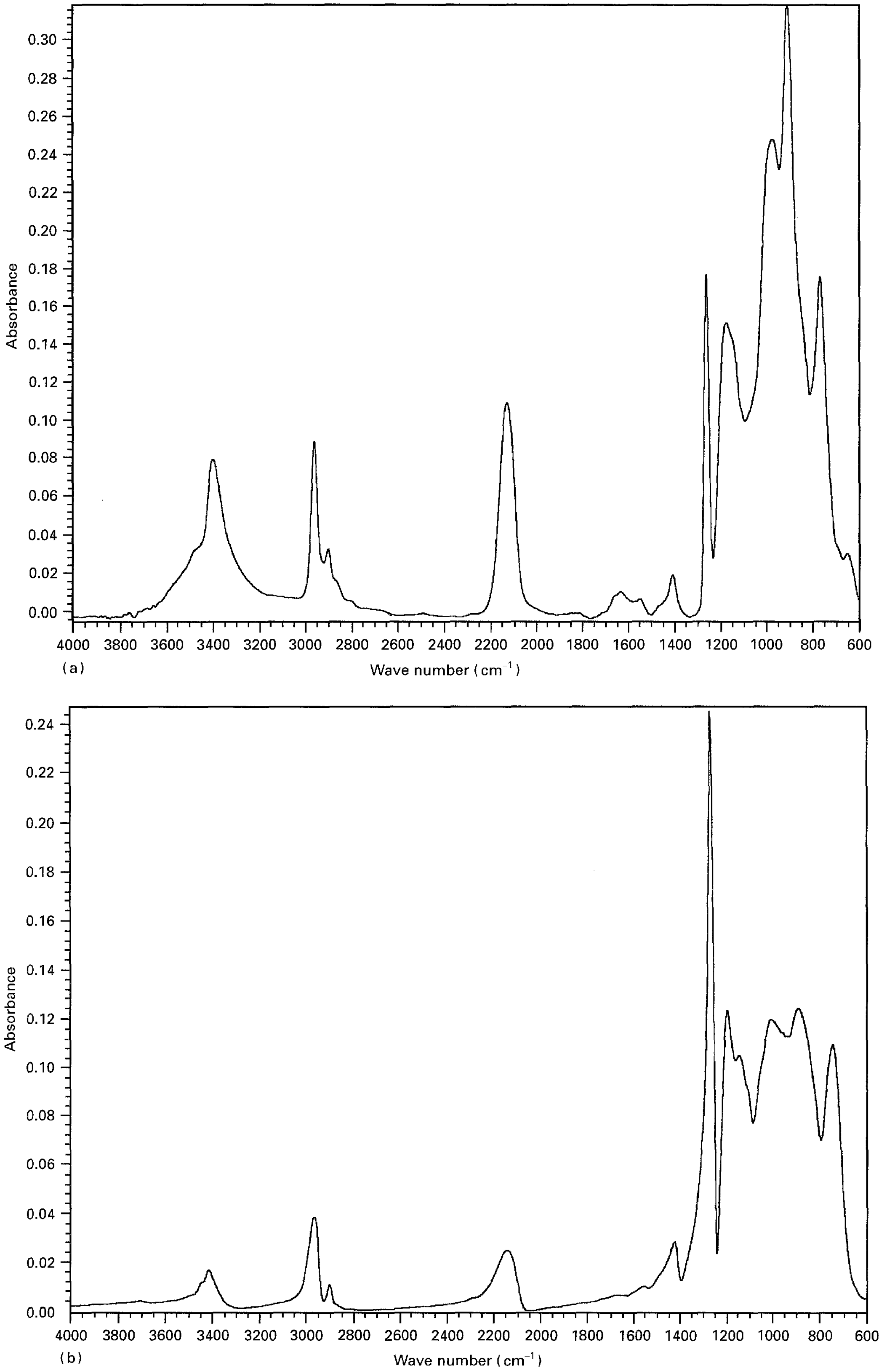
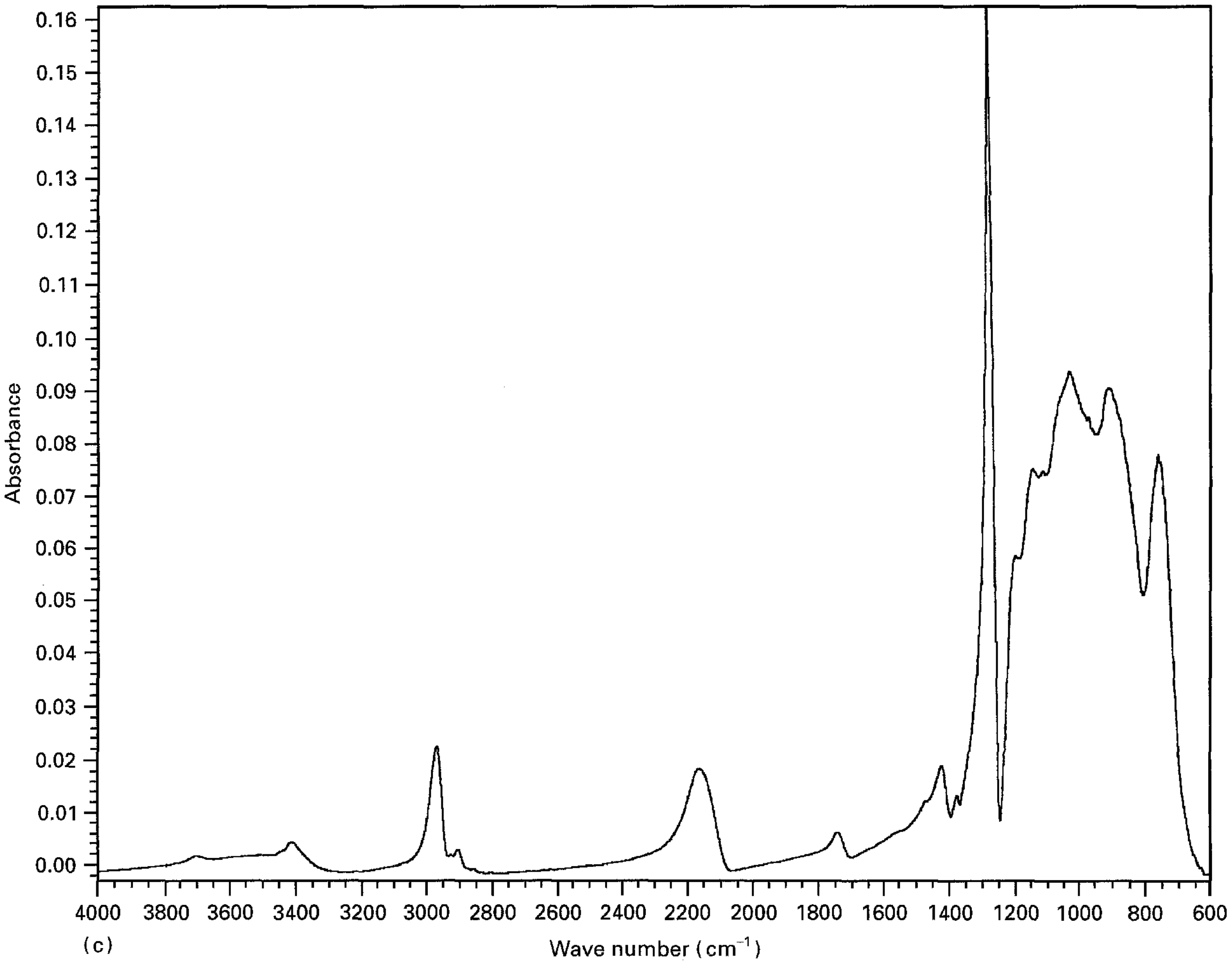
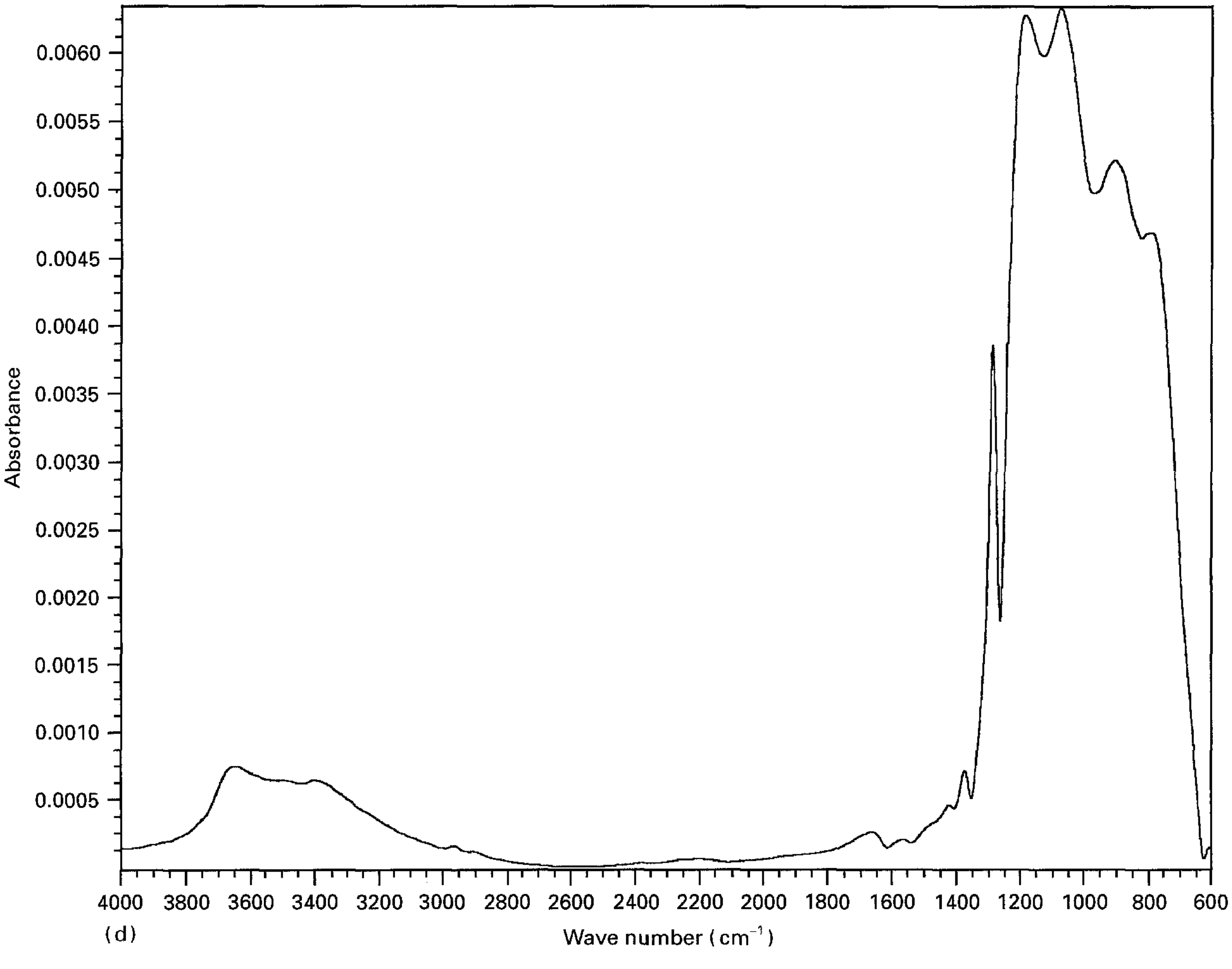


Figure 7 FT–IR spectra of (a) the copolymer P11B; (b) residue after pyrolysis in nitrogen to 450 °C; (c) residue after pyrolysis in nitrogen to 500 °C; (d) residue after pyrolysis in nitrogen to 800 °C; (e) residue after pyrolysis in nitrogen to 980 °C.


Absorbance
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wave number (cm^{-1})

(c)


Absorbance
0.0060
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wave number (cm^{-1})

(d)

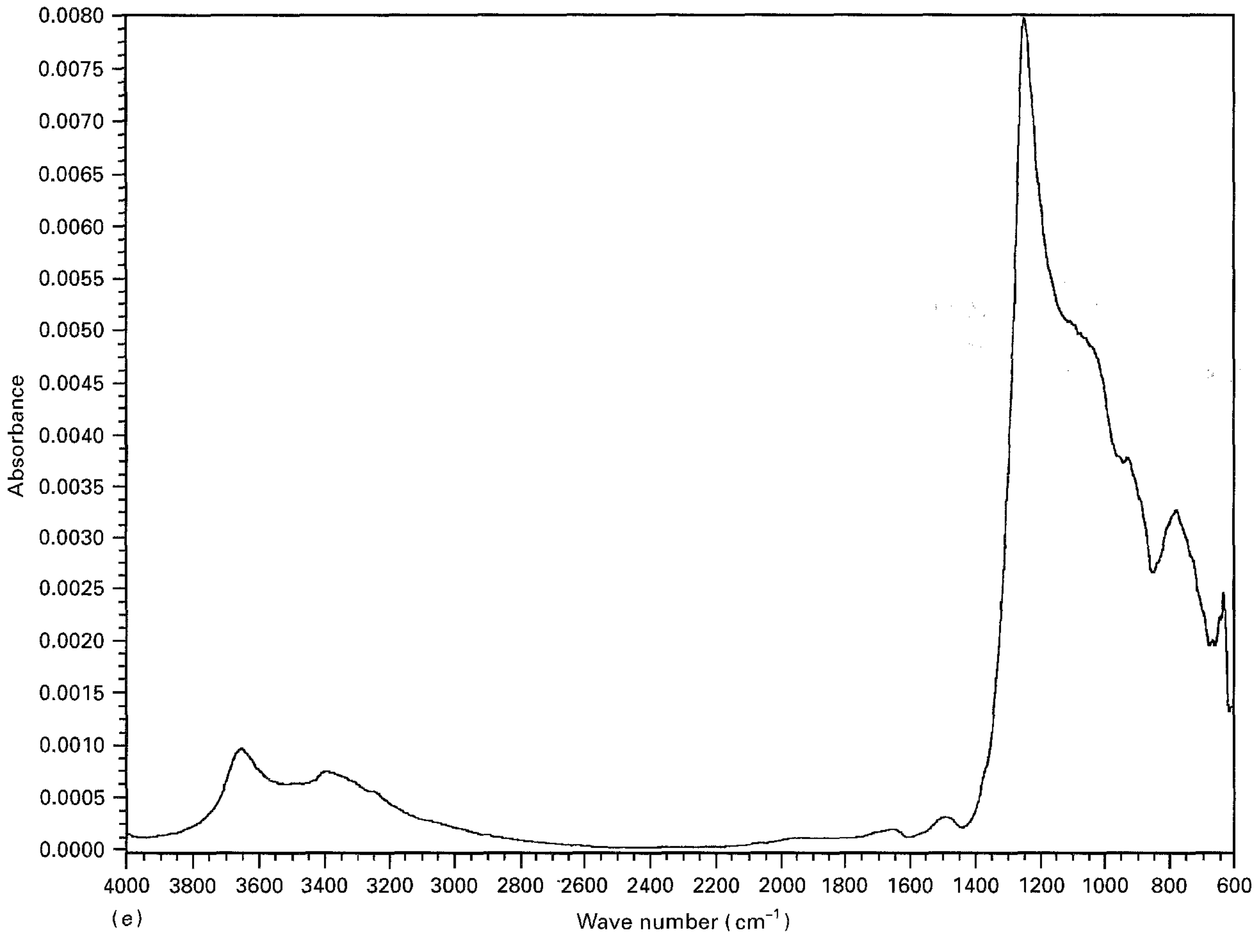
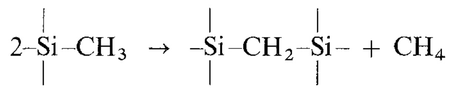


Figure 7 Continued.

The decomposition of copolymer P11B in nitrogen (used in further studies as described in section 3.2 *et seq.*) has been analysed using FT–IR of the residue at various stages during pyrolysis. The FT–IR spectrum of the residue obtained after heating to 400 °C (Fig. 7(b)) in comparison with the spectrum of the copolymer (Fig. 7(a)) shows that the N–H stretching ($3400\,\mathrm{cm^{-1}}$), and Si–H stretching ($2140\,\mathrm{cm^{-1}}$) peaks diminish in intensity compared with the Si–CH_3 (1258, 898, $764\,\mathrm{cm^{-1}}$) and CH_3 (2968, $1400\,\mathrm{cm^{-1}}$) peaks. This is caused by the release of ammonia at about 400 °C [9]. Comparison of the spectrum in Fig. 7(c) at 500 °C when the release of methane just begins [9] with that in Fig. 7(d) at 800 °C when the evolution of methane is near completion shows that in the latter instance the Si–H peak has virtually disappeared and the intensity of the CH_3 peaks have decreased appreciably. At 980 °C (Fig. 7(e)), the CH_3 peaks have virtually disappeared but a small N–H peak remains and the absorption peak at $1490\,\mathrm{cm^{-1}}$ corresponds to the formation of the Si–O–N structure.

It is noteworthy that during the evolution of methane from the copolymer, i.e. from about 500 °C until about 800 °C (FT–IR spectrum in Fig. 7(c) and (d)), the Si–CH_2–Si peak (approximately $1370\,\mathrm{cm^{-1}}$) can be seen. In our previous work [9, 10] we presented a series of reactions that take place during the pyrolytic decomposition of a similar copolymer in nitrogen. The reaction given below was suggested and is now supported by the presence of the Si–CH_2–Si peak as explained above.



$$2\text{–}\underset{|}{\overset{|}{\mathrm{Si}}}\text{–}\mathrm{CH_3} \rightarrow \text{–}\underset{|}{\overset{|}{\mathrm{Si}}}\text{–}\mathrm{CH_2}\text{–}\underset{|}{\overset{|}{\mathrm{Si}}}\text{–} + \mathrm{CH_4}$$

The Si–CH_2–Si structure was also observed by Han and coworkers [11] during the pyrolysis of polyorganosilazanes.

3.2. Pyrolysis in the tube furnace

It was clear from the thermogravimetric studies that the use of ammonia in the pyrolysis atmosphere had a significant effect on the colour of the residue (Table II). In ammonia/nitrogen mixtures the colour of the pyrolysis residue was grey/white for all the copolymers whilst in nitrogen a black residue was obtained in each case.

Pyrolysis of about 1 g of copolymer P11B in the tube furnace (as opposed to a few mg in the thermogravimetric balance) enabled the preparation of a larger quantity of residue. These experiments showed clearly that the atmosphere used during pyrolysis had a significant influence on the residue. When nitrogen was used, pyrolysis at 1000 °C produced a black, amorphous residue. Crystallization at 1600 °C and characterization by XRD has shown that the product was a very pure form of αSi_3N_4 and this work has

TABLE III Weight % of weight residue obtained by pyrolysis of copolymer P11B in ammonia during a predetermined temperature range. Nitrogen was used at all other temperatures

Temperature range (°C)	300–400	400–500	500–600	600–700	700–800	800–900
White residue content (wt %)	0	< 2	> 60	> 75	< 2	0

been discussed separately [10]. However, if pyrolysis was carried out in nitrogen, except over a predetermined temperature range when nitrogen was replaced by ammonia, varying amounts of a white, amorphous residue (Si_2ON_2) was obtained. Therefore, the pyrolysis atmosphere can be varied according to the pyrolysis temperature to synthesize different ceramics. It is widely known that both nitrogen and ammonia remove carbon from the polymeric precursor but the latter does it more efficiently [5]. In addition, pyrolysis of copolymers prepared using siloxanes and silazanes in ammonia allows the retention of oxygen and this allows the synthesis of nitrogen ceramics such as Si_2ON_2 [6]. However, the present work shows that ammonia is required only over a certain range of temperature and that this range can be optimized as discussed below.

Table III shows that the proportion of white residue was dependent on the temperature range pyrolysis was carried out in the presence of an ammonia atmosphere. In fact, further experimentation showed that pyrolysis in an ammonia atmosphere in the temperature range 500–700 °C produced the white, amorphous residue in increased yield (> 95%). The introduction of ammonia during this temperature range allows the retention of both oxygen and nitrogen in the sample. Crystallization of the residue obtained using the above-described procedure at 1600 °C and subsequent characterization by XRD (Fig. 8) showed that the residue was Si_2ON_2. The *d*-spacing data deduced from the XRD spectrum (Fig. 8) are shown in Table IV and these agree with those expected from Si_2ON_2 [12, 13].

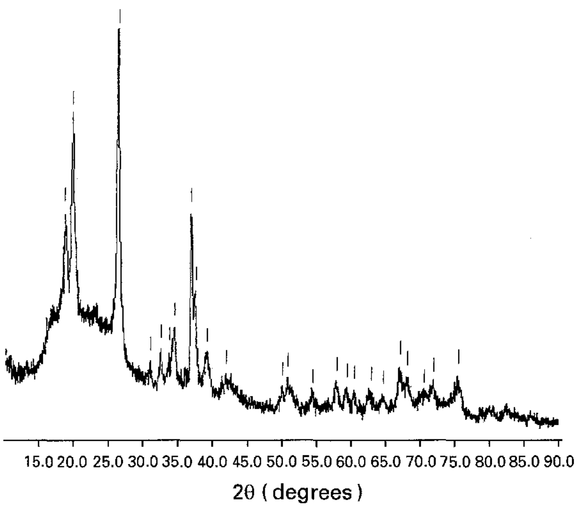


Figure 8 XRD spectrum of the silicon oxynitride powder synthesized in the present work.

TABLE IV Data deduced from the XRD spectrum shown in Fig. 8

2θ	*d*-spacing	Relative intensity
19.01	4.664	55
20.11	4.412	80
26.54	3.356	100
31.11	2.872	19
32.66	2.740	22
33.79	2.650	21
34.57	2.593	27
37.07	2.423	55
37.63	2.388	36
39.33	2.289	21
42.05	2.147	16
50.21	1.815	13
51.02	1.789	15
54.48	1.683	11
57.91	1.591	15
59.42	1.554	13
60.49	1.529	12
62.89	1.477	12
64.74	1.439	11
67.18	1.392	18
68.19	1.374	16
70.72	1.331	12
72.08	1.309	15
75.47	1.259	16

3.3. Crystallization and powder characteristics

The heat treatment of the residue obtained from pyrolysis of the copolymer is a crucial stage in the synthesis of the ceramic. FT–IR shows that the amorphous residue (as verified by XRD) contains peaks related to aliphatic carbon atoms (Fig. 9(a)) while after crystallization (as verified by XRD – see Fig. 8) only the characteristic peak of Si_2ON_2 is present (Fig. 9(b)). The crystallization heat treatment described in section 2.4 was adopted after a series of exploratory experiments. The product after crystallization is also affected significantly by the oxygen and moisture content in the atmosphere and the carbon content in the amorphous residue. A high C:O ratio in the residue results in the consumption of the oxygen during crystallization and Si_3N_4 is produced. A low C:O ratio helps to produce Si_2ON_2.

Crystallization at a higher temperature (1660 °C compared with 1600 °C) for a much longer time (5 h compared with 2 h at 1600 °C) resulted in a Si_2ON_2–Si_3N_4 mixture being produced as verified by XRD. Thus, the temperature and time used in the crystallization heat treatment can be varied to produce a different ceramic and offers possibilities for the controlled production of ceramic composites.

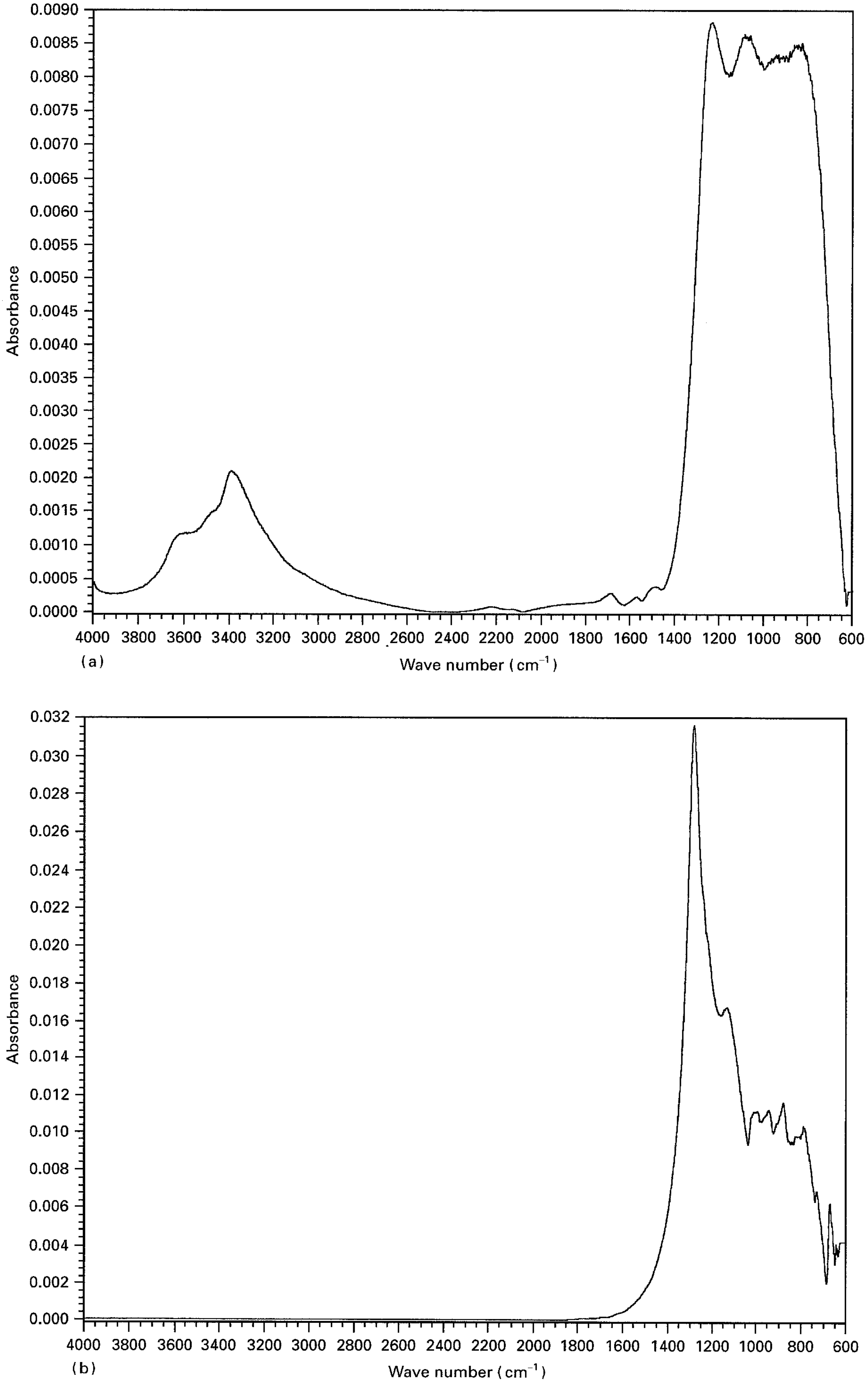


Figure 9 FT–IR spectra of the silicon oxynitride powder synthesized in the present work. (a) Residue after pyrolysis; (b) residue after crystallization.

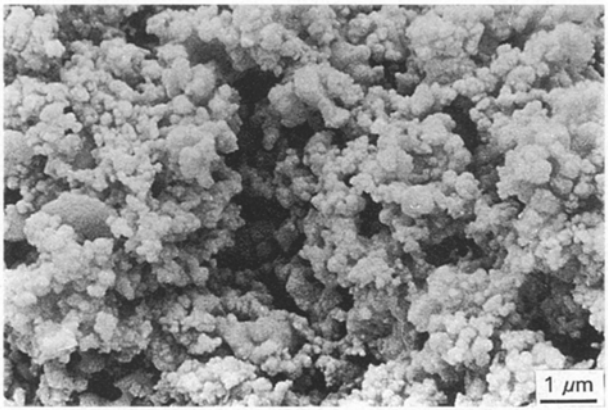


Figure 10 Scanning electron micrograph of the silicon oxynitride powder synthesized in the present work.

The silicon oxynitride synthesized (Fig. 10) contained equiaxed particles in the size range 50–150 nm. However, these particles were within agglomerates of 0.3–0.1 μm in size.

4. Conclusions

Thermogravimetry of different copolymers prepared using methylcyclosiloxanes and methylcyclosilazanes in nitrogen, an ammonia/nitrogen mixture, air and oxygen have shown that the temperatures at which decomposition occurs, the weight of ceramic residue and the rate of weight loss can be varied appreciably by changing the pyrolysis atmosphere. However, the method of preparation and the chemical structure of the copolymers can also influence these three parameters.

Further investigation of the residue obtained at various stages of the pyrolysis in nitrogen of one of the copolymers using FT–IR has shown that the ceramic starts to evolve from the copolymer at about 400 °C by the release of ammonia followed by the loss of methane at about 500 °C. Pyrolysis of this copolymer on a larger scale has shown clearly that the ceramic synthesized is dependent crucially on the pyrolysis atmosphere used. Pyrolysis in nitrogen at 1000 °C produced αSi_3N_4. Pyrolysis in ammonia instead of nitrogen in the temperature range 500–700 °C produced Si_2ON_2 with a yield of > 95 wt %.

The Si_2ON_2 synthesized in this manner was amorphous and after crystallization by heating further to 1600 °C gave Si_2ON_2 crystals in the size range 50–150 nm. The crystallization temperature of the amorphous pyrolysis residue also played an important part in the synthesis of the ceramic required. Although Si_2ON_2 crystals were obtained by heating to 1600 °C, heat treatment at 1660 °C resulted in the synthesis of αSi_3N_4–Si_2ON_2 mixtures.

Acknowledgements

We are grateful to SERC for providing financial support for this project (grant ref. GR/H09904). Assistance in thermogravimetric studies and X-ray diffraction work provided by Dr S. Woodisse is acknowledged gratefully. Dr T. Zhang and Dr A. Jha are thanked for valuable discussions on the crystallization experiments. Mrs K. Goddard is thanked for typing this manuscript.

References

1. GA-ER YU, J. PARRICK, M. EDIRISINGHE, D. FINCH and B. RALPH, *J. Mater. Sci.* **28** (1993) 4250.
2. *Idem, ibid.* **29** (1994) 1680.
3. *Idem, ibid.* **29** (1994) 5569.
4. D. SEYFERTH, G. H. WISEMAN, C. A. PONTASSE, J. M. SCHWARK and Y-F. YU, *Polym. Prepr. (Div. Polym. Chem., Amer. Chem. Soc.)* **28** (1987) 389.
5. Y. D. BLUM, G. A. McDERMOTT, R. B. WILSON and A. S. HIRSCHON, *ibid.* **32** (1991) 548.
6. Y. YU and T. MAH, in Proceedings of the Materials Research Society Symposium, edited by J. Brinker, D. E. Clark and D. R. Ulrich, Materials Research Society, Pittsburgh, PA, USA, 1986, p. 559.
7. G. T. BURNS and G. CHANDRA, *J. Amer. Ceram. Soc.* **72** (1989) 333.
8. O. FUNAYAMA, T. KATO, Y. TASHIRO and T. ISHODA, *ibid.* **76** (1993) 717.
9. GA-ER YU, D. S. FINCH, M. J. EDIRISINGHE, J. PARRICK and B. RALPH, in Proceedings of the Materials Research Society Symposium, edited by A. R. Barron, G. S. Fischman, M. A. Fury and A. F. Hepp, Materials Research Society, Pittsburgh, PA, USA, 1994, vol. 327, p. 201.
10. GA-ER YU, M. J. EDIRISINGHE, D. S. FINCH, B. RALPH and J. PARRICK, *J. Euro. Ceram. Soc.* **15** (1995) 581.
11. H. N. HAN, D. A. LINQUIST, J. S. HAGGARTY and D. SEYFERTH, *Chem. Mater.* **4** (1992) 705.
12. I. IDRESTEDT and C. BROSSET, *Acta Chem. Scand.* **18** (1964) 1886.
13. N. SJØBERS, *Acta Cryst.* **C47** (1991) 2438.

Received 17 March
and accepted 11 April 1995