

# Method for Preparing Polyaluminocarbosilane

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Received 1 April 2008; accepted 26 January 2009

DOI 10.1002/app.30153

Published online 14 May 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyaluminocarbosilane (PACS) was synthesized directly by the one-pot reaction of polydimethylsilane (PDMS) with aluminum acetylacetonate [Al(acac)<sub>3</sub>] in an autoclave. In this closed system, all the aluminum in Al(acac)<sub>3</sub> was converted into PACS. Therefore, the content of aluminum could be readily controlled quantitatively. On the basis of Fourier transform infrared, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>29</sup>Si-NMR, and <sup>27</sup>Al magic-angle spinning NMR analysis, the reaction mechanism was proposed as follows: PDMS dissociated during pyrolysis to generate silicon free radicals, and then they reacted with Al(acac)<sub>3</sub> to yield PACS containing (Si—O)<sub>n</sub>Al groups (*n* = 4, 5, or 6). Mean-

while, these reactions resulted in the cleavage of O—C and/or O=C bonds in Al(acac)<sub>3</sub>. Some of the free-radical fragments generated by this cleavage continued to react with the silicon free radicals and were incorporated into the structural units of PACS; the rest of them may have been converted into small oxygen-containing compounds, which were removed in the subsequent processing after the reactions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3725–3731, 2009

**Key words:** heteroatom-containing polymers; polysilanes; synthesis

## INTRODUCTION

Polycarbosilane (PCS) has been developed as a successful preceramic polymer for the industrial production of SiC fibers during the past 30 years on the basis of the pioneering work of Yajima and coworkers in the 1970s.<sup>1–4</sup> Moreover, various kinds of polymetallocarbosilanes have been developed by the incorporation of metal elements such as titanium,<sup>5–8</sup> zirconium,<sup>9–12</sup> tantalum,<sup>13</sup> and aluminum,<sup>14–20</sup> into PCS to improve the thermal resistance of SiC fibers and ceramics. Polymetallocarbosilanes have been also developed as important preceramic polymers for functional gradient materials<sup>21–23</sup> and gas-separation membranes.<sup>24</sup>

Recently, polyaluminocarbosilane (PACS) was used as a preceramic polymer to produce Tyranno SA fiber, an aluminum-containing sintered SiC fiber reported to have high strength and alkali resistance and be thermally stable up to 2200°C.<sup>15</sup> PACS is prepared through the reaction of PCS with aluminum acetylacetonate [Al(acac)<sub>3</sub>] at 300°C in nitrogen at the ambient pressure. Aluminum plays a very important role as a sintering aid to ensure that the SiC fiber maintains its form and strength when sintered at a

high temperature (1800°C), whereas the Si—C—O fiber will decompose into powdery materials under such conditions.<sup>25</sup> It is essential to control the content of aluminum in PACS so that the SiC fiber can reach a high density. Li and coworkers<sup>26</sup> found that it is very hard to reproduce PACS with a controlled content of aluminum because Al(acac)<sub>3</sub> tends to sublime around 300°C under the ambient pressure. They replaced the starting material PCS with polysilacarbosilane, a liquid product synthesized by the thermolysis of polydimethylsilane {PDMS or [(Me)<sub>2</sub>Si]<sub>n</sub>} at 340–360°C under the ambient pressure.<sup>27</sup> The sublimation of Al(acac)<sub>3</sub> can be alleviated significantly but cannot be avoided completely. It is still difficult to reproduce PACS with a controlled content of aluminum according to Yu et al.<sup>28</sup> In their method, a two-step reaction is needed: both PCS and polysilacarbosilane are prepared from PDMS, and then PCS or polysilacarbosilane is converted into PACS. The content of aluminum in PACS must be controlled so that the aluminum content in the final SiC(Al) fiber is below 2 wt % to ensure the best performance of the resultant fiber.<sup>15</sup> This prompted us to develop a new method to prepare PACS for SiC(Al) fibers by a one-pot reaction of PDMS with Al(acac)<sub>3</sub> in an autoclave. In this article, we report the preparation procedures and the reaction mechanism of PACS.

## EXPERIMENTAL

### Materials

PDMS (Xinhuo Chemical Plant, China, Changsha, China), 95% ethanol, ethyl formate (Sinopharm

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Contract grant sponsor: Natural Science Foundation of Fujian Province of China; contract grant number: 2008J0165.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50532010.

Chemical Reagent, Shanghai, China), and  $\text{Al}(\text{acac})_3$  (Stream) were all used as purchased. Dry hexane was obtained through distillation under nitrogen from sodium benzophenone. PCS was prepared according to the literature procedure.<sup>4</sup>

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer (Waltham, MA) with the KBr pellet method. Solution NMR experiments were performed on a Bruker Advance II-300 spectrometer ( $^1\text{H}$ , 300 MHz;  $^{13}\text{C}$ , 75.5 MHz; and  $^{29}\text{Si}$ , 59.6 MHz) at room temperature in  $\text{CDCl}_3$ . The inverse-gated  $^{29}\text{Si}$ -NMR spectra were recorded with a pulse delay time of 28 s. Tetramethylsilane (0 ppm) was used as the external standard for  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR chemical shifts.  $^{27}\text{Al}$  magic-angle spinning (MAS) NMR spectra of PACS were obtained on a Bruker Advance II-300 spectrometer at 78.2 MHz with a Bruker 4.0-mm MAS BB probe. The spinning rate was 12.0 kHz. The  $^{27}\text{Al}$  chemical shift was referenced to 1.5M aqueous  $\text{Al}(\text{NO}_3)_3$  (0 ppm).

The number-average molecular weight was estimated with a gel permeation chromatograph (series 1100, Agilent, Santa Clara, CA). It was equipped with a refractive-index detector and gel columns (Styragel HR 3 and HR 1, Waters). Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The gel columns were calibrated with narrow-molecular-weight polystyrene standards (polydispersity index  $\leq 1.05$ ; Shoko, Japan).

The aluminum content was measured by the chemical method described in the literature.<sup>29</sup> The oxygen content was determined with an oxygen-nitrogen element analyzer (EMGA-620W, Horiba, Kyoto, Japan).

### General procedures for the preparation of PACS

A typical experiment for preparing PACS for  $\text{SiC}(\text{Al})$  fiber was as follows:  $\text{Al}(\text{acac})_3$  (2.0 g) and PDMS (50.0 g) were mixed and charged into a 300-mL autoclave (EZE-seal, Autoclave Engineers, Erie, PA). The autoclave was then degassed and refilled with argon three times at room temperature. The temperature was then increased to 450°C (2°C/min) and main-

tained there for 6 h. The final pressure inside the container was about 9.0 MPa. After the reaction, dry hexane (120 mL) was introduced into the container to dissolve the product. The resultant solution was filtered to remove the insoluble byproduct. Finally, the solvent of the filtrate was evaporated and dried *in vacuo* at 60°C to yield 37.5 g of PACS as a yellow solid (PACS-N).

### Preparation of PACS for the mechanism study

To investigate the mechanism of PACS formation, the ratio of  $\text{Al}(\text{acac})_3$  to PDMS was deliberately increased:  $\text{Al}(\text{acac})_3$  (10.0 g) and PDMS (40.0 g) were mixed and charged into a 300-mL autoclave (EZE-seal, Autoclave Engineers). The autoclave was then degassed and refilled with argon three times at room temperature. The temperature was then increased to 450°C (2°C/min) and maintained there for 0.5 h. The final pressure inside the container was about 6.5 MPa. After the reaction, dry hexane (120 mL) was introduced into the container to dissolve the product. The resultant solution was filtered to remove the insoluble byproduct. Finally, the solvent of the filtrate was evaporated and dried *in vacuo* at 60°C to yield 36.2 g of PACS as a yellow solid (PACS-M).

## RESULTS AND DISCUSSION

### Contents of aluminum and oxygen in PACS

Because the reaction is conducted in an autoclave, the sublimation of  $\text{Al}(\text{acac})_3$  is prevented. As shown in Table I, almost all the aluminum in  $\text{Al}(\text{acac})_3$  is incorporated into PACS. The yield of PACS from PDMS is essentially constant:  $\sim 73\%$ . Therefore, the content of aluminum in PACS can be readily calculated. Table I shows clearly that the measured aluminum content is in very good agreement with the calculated value. However, the measured oxygen content in PACS is less than the calculated value, and this indicates that some oxygen-containing compounds are lost as exhaust gas in the subsequent processing after the reaction.

Ethyl formate and 95% ethanol are used to extract the low-molecular-weight fragments of PACS. After extraction, the remaining insoluble product of

TABLE I  
Contents of Aluminum and Oxygen in PACS

Al(acac) <sub>3</sub> /PDMS (g/g)	PACS yield (%)	Aluminum (%)		Oxygen (%)	
		Measured	Calculated	Measured	Calculated
2.0/50.0	72	0.47	0.44	1.3	1.5
3.0/50.0	73	0.68	0.64	1.5	2.3
4.0/50.0	74	0.80	0.83	1.8	2.9
6.0/50.0	74	1.1	1.2	2.6	4.3

**TABLE II**  
Effect of the Solvent Treatment on the Number-Average Molecular Weight ( $M_n$ ) Values and Aluminum and Oxygen Concentrations of PACS-N

Treatment of PACS-N	$M_n$ ( $\times 10^3$ )	Aluminum (%)	Oxygen (%)
Raw (no treatment)	1.17	0.48	1.3
95% ethanol	1.45	0.54	1.4
Ethyl formate	3.62	0.84	2.0

PACS-N is collected by filtration and dried *in vacuo* at 60°C. As shown in Table II, the number-average molecular weight of PACS and the contents of aluminum and oxygen increase after extraction. This shows that aluminum is successfully introduced into the structural units of PACS by the one-pot reaction.

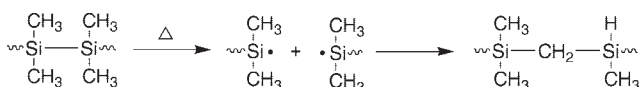
### Proposed mechanism of PACS formation

The conversion of PDMS to PCS by thermal decomposition is referred to as the well-known Kumada rearrangement.<sup>4,30</sup> According to this mechanism, a silicon free radical is formed first when the Si—Si bond is cleaved by heating, and this is followed by rearrangement involving the insertion of a methylene group into the Si—Si chain to yield Si—CH<sub>2</sub>—Si and Si—H groups (Scheme 1). The Si—H group can be detected in the FTIR spectrum around 2100 cm<sup>-1</sup> [Si—H stretching; Fig. 1(A)].<sup>4</sup>

In this work, when the ratio of Al(acac)<sub>3</sub> to PDMS is 1/25, no additional absorptions are observed in the resultant PACS-N [Fig. 1(B)] in comparison with PCS [Fig. 1(A)]. One possible reason is that the content of aluminum in PACS-N is so low that the absorption of Al—X (X = O, Si, or C) is undetectable. This may be also due to the overlapping of the Al—X absorption with the other existing peaks.

To clarify the aforementioned questions, the ratio of Al(acac)<sub>3</sub> to PDMS was increased to 1/4. The PACS so formed is designated PACS-M. As shown in the FTIR spectrum [Fig. 1(C)], the strength of absorption at 2100 (Si—H stretching) and 2898 cm<sup>-1</sup> (—CH<sub>2</sub>— stretching) has decreased, and this indicates that the formation of Si—H and Si—CH<sub>2</sub>—Si groups from silicon free radicals through Kumada rearrangement is impeded by the presence of Al(acac)<sub>3</sub>.

The reduction of Si—H groups is also confirmed by its low content of Si—H fragments (3.6–4.8 ppm)<sup>4</sup> in the <sup>1</sup>H-NMR spectrum of PACS-M [Fig. 2(B)]. In



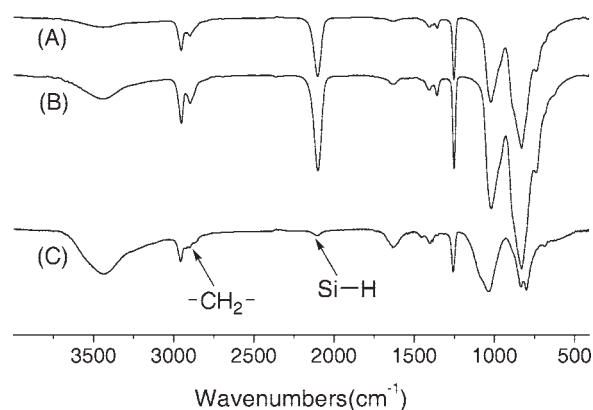
**Scheme 1** Kumada rearrangement of PCS formation.

addition, in comparison with PACS-N [Fig. 2(A)], several new broad peaks between 0.8 and 2.4 ppm are found in PACS-M, and these can be assigned to alkyl groups. The appearance of additional alkyl groups indicates that they must originate from the fragments of the ligand in Al(acac)<sub>3</sub>. However, no obvious signals corresponding to O—C (45–95 ppm) or O=C (145–230 ppm) groups<sup>31</sup> in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of PACS-M [Fig. 3(B)] can be observed. Therefore, the cleavage of O—C and/or O=C groups in Al(acac)<sub>3</sub> must have occurred. The cleavage of O—C and/or O=C groups in Al(acac)<sub>3</sub> was also reported when PCS<sup>26</sup> was used as the starting material.

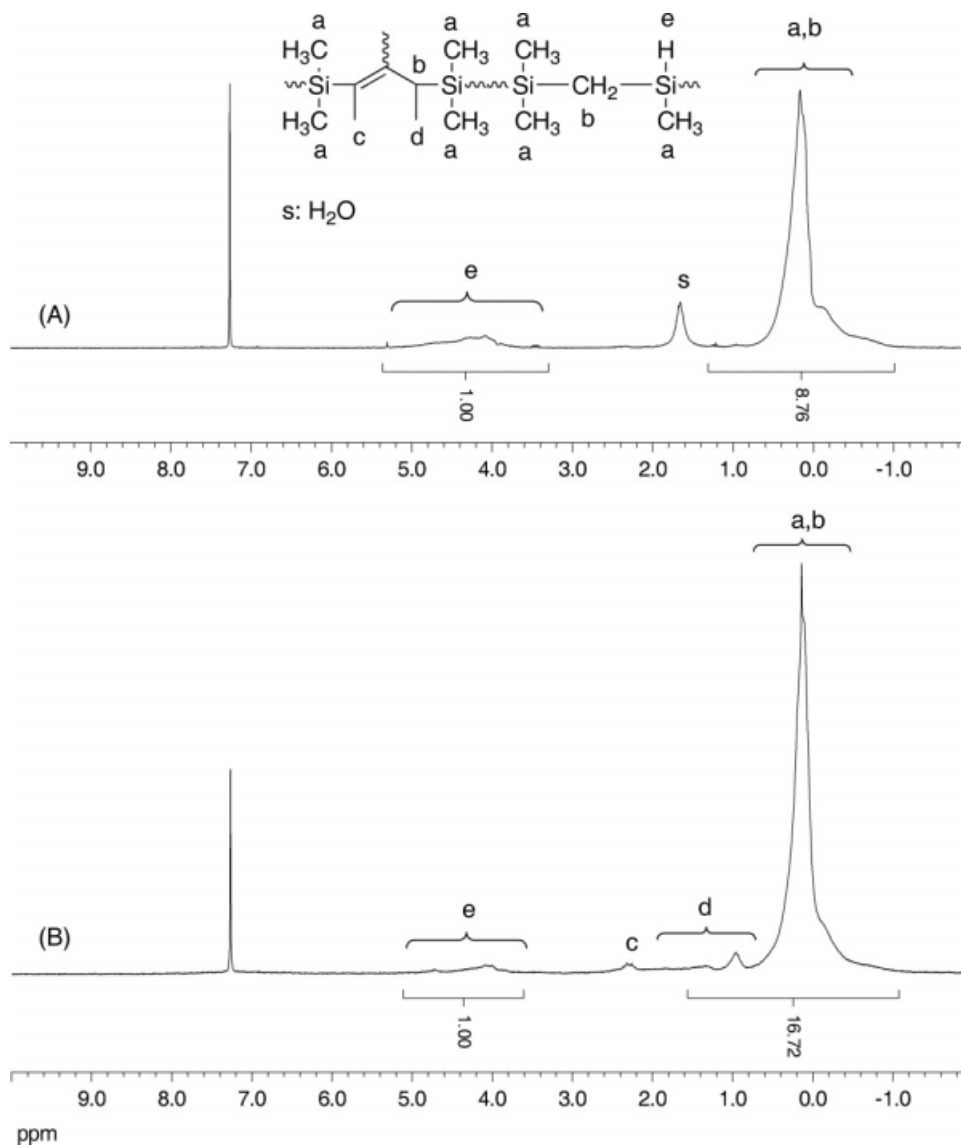
As shown in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of PACS-N [Fig. 3(A)], the peak between -10 and 15 ppm is attributable to Si—CH<sub>3</sub> and Si—CH<sub>2</sub>—Si groups. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of PACS-M is shown in Figure 3(B). The signal between 15 and 30 ppm [Fig. 3(B)] confirms the presence of alkyl groups in PACS-M, and this is in agreement with the <sup>1</sup>H-NMR analysis. The broad peaks between 115 and 145 ppm [Fig. 3(B)] are assigned to unsaturated C=C groups. These unsaturated C=C groups must also originate from the fragments of the ligand in Al(acac)<sub>3</sub>. In addition, the disappearance of most of the signals (115–145 ppm) in the <sup>13</sup>C distortionless enhancement by polarization transfer (DEPT) 135 spectrum of PACS-M [Fig. 3(C)] indicates that most of the carbon atoms in unsaturated C=C groups should exist as quaternary carbons.

Moreover, the small peak around 22 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum [Fig. 3(B)] can be assigned to methyl in —C=C—CH<sub>3</sub> groups, whose protons are located at 2.2–2.4 ppm in the <sup>1</sup>H-NMR spectrum [Fig. 2(B)].

The inverse-gated <sup>29</sup>Si-NMR spectra of PACS are shown in Figure 4. The peaks are located mainly in four regions. They are assigned to the following groups on the basis of previous work:<sup>30,32,33</sup> OSiC<sub>3</sub>



**Figure 1** FTIR spectra of (A) PCS, (B) PACS-N, and (C) PACS-M.



**Figure 2**  $^1\text{H}$ -NMR spectra of (A) PACS-N and (B) PACS-M in  $\text{CDCl}_3$ .

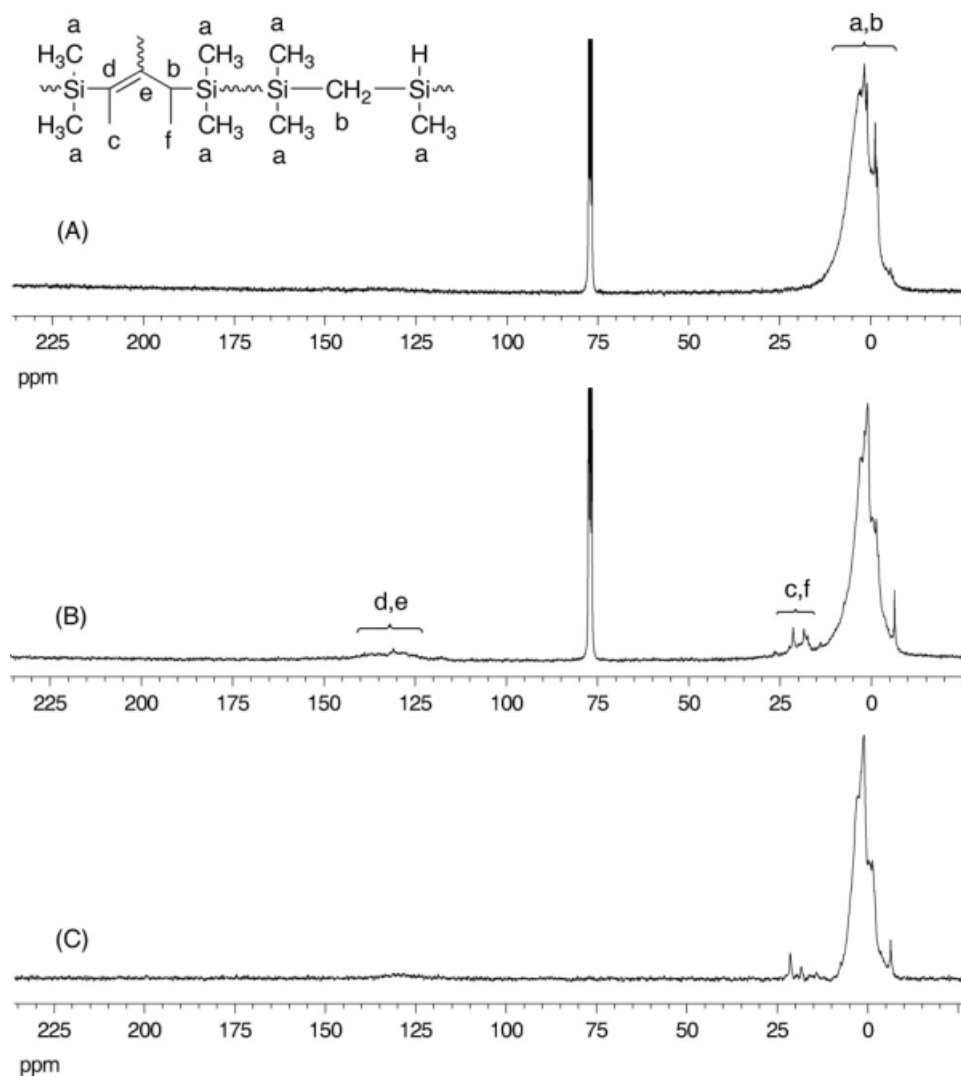
(5–20 ppm),  $\text{SiC}_4$  (–5 to 5 ppm), H–Si ( $\text{HSiC}_3$  and  $\text{OSiHC}_2$ ; –20 to –10 ppm), and Si–Si (–45 to –30 ppm). The broad peak between –140 and –75 ppm is due to  $\text{SiO}_2$  in the glass NMR tube. In comparison with PACS-N [Fig. 4(A)], the signals situated at 5–20 ppm and at –12 to –6 ppm in PACS-M [Fig. 4(B)] are enhanced. They are attributable to O–Si groups ( $\text{OSiC}_3$  and  $\text{OSiHC}_2$ ). This indicates that most of the formed silicon free radicals have been converted into O–Si groups.

There are three peaks in the  $^{27}\text{Al}$  MAS NMR spectra of PACS (Fig. 5). They are located at 0, 30, and 60 ppm and are assigned to  $\text{AlO}_6$ ,  $\text{AlO}_5$ , and  $\text{AlO}_4$  sites,<sup>19</sup> respectively.

Therefore, the formation of Si–O and  $\text{AlO}_n$  ( $n = 4, 5, \text{ or } 6$ ) groups, which is believed to be the result of the cleavage of C–O and/or C=O groups in Al

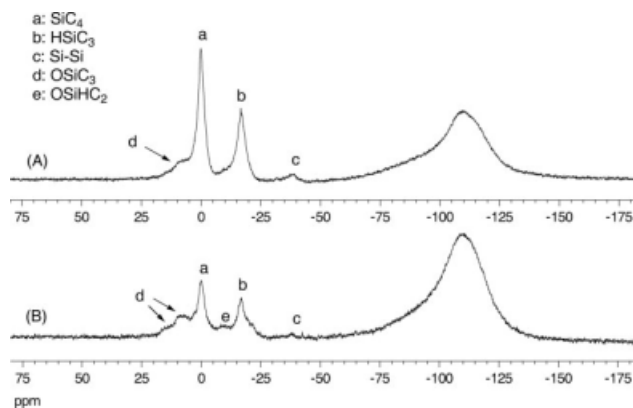
( $\text{acac}$ )<sub>3</sub> during the Kumada rearrangement, can be described as follows (Scheme 2). Silicon-free radicals, which are generated from the pyrolysis of PDMS, react with  $\text{Al}(\text{acac})_3$  to produce PACS containing  $(\text{Si}-\text{O})_n\text{Al}$  groups ( $n = 4, 5, \text{ or } 6$ ). In this way, all the aluminum in  $\text{Al}(\text{acac})_3$  is converted into PACS [Scheme 2(A)]. Meanwhile, this reaction is accompanied by the cleavage of O–C and/or O=C bonds in  $\text{Al}(\text{acac})_3$  and generates small free-radical fragments simultaneously. The small free-radical fragments cannot escape the closed reaction system. Some of them are incorporated into the molecular structure of PACS [detectable by  $^{13}\text{C}\{^1\text{H}\}$  NMR; Fig. 3(B)] in the regions of 115–145 and 15–35 ppm; the rest of them may be converted into small oxygen-containing compounds [Scheme 2(B)], which are removed in the subsequent processing after the reaction. This





**Figure 3** (A,B)  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of PACS-N and PACS-M, respectively, and (C)  $^{13}\text{C}$  DEPT 135 NMR spectrum of PACS-M in  $\text{CDCl}_3$ .

results in reduced oxygen content in the final product. That is why the measured content of oxygen in PACS is less than the calculated value.



**Figure 4** Inverse-gated  $^{29}\text{Si}$ -NMR spectra of (A) PACS-N and (B) PACS-M in  $\text{CDCl}_3$ .

## CONCLUSIONS

PACS was synthesized directly by the one-pot reaction of PDMS with  $\text{Al}(\text{acac})_3$  in an autoclave. The content of aluminum in PACS could be readily controlled quantitatively. The reaction mechanism was proposed as follows: PDMS dissociated during pyrolysis to generate silicon free radicals, and then  $\text{Al}(\text{acac})_3$  reacted with the silicon free radicals to produce PACS, which contained  $(\text{Si}-\text{O})_n\text{Al}$  groups with  $\text{AlO}_6$ ,  $\text{AlO}_5$ , and  $\text{AlO}_4$  sites. These reactions resulted in the cleavage of  $\text{O}-\text{C}$  and/or  $\text{O}=\text{C}$  bonds in  $\text{Al}(\text{acac})_3$  and generated small free-radical fragments simultaneously. Some of the fragments were incorporated into the structural units of PACS; the rest of them may have been converted into small oxygen-containing compounds, which were removed in the subsequent processing after the reactions. This reduced the content of oxygen in PACS.

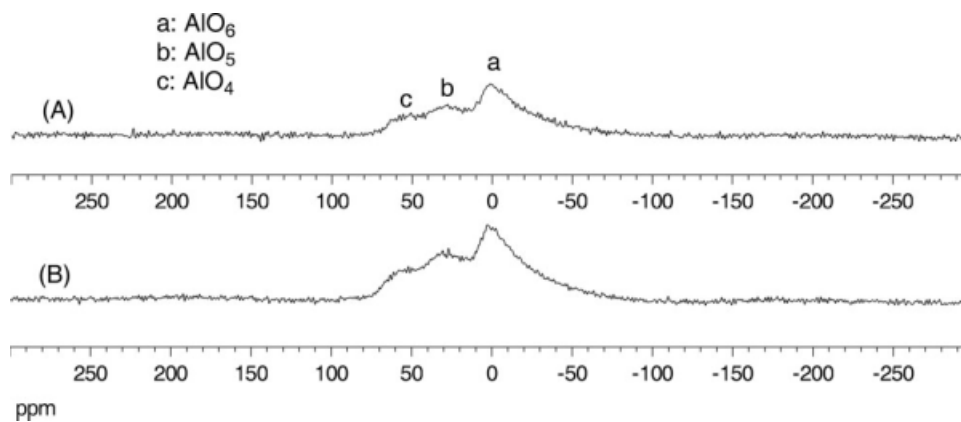
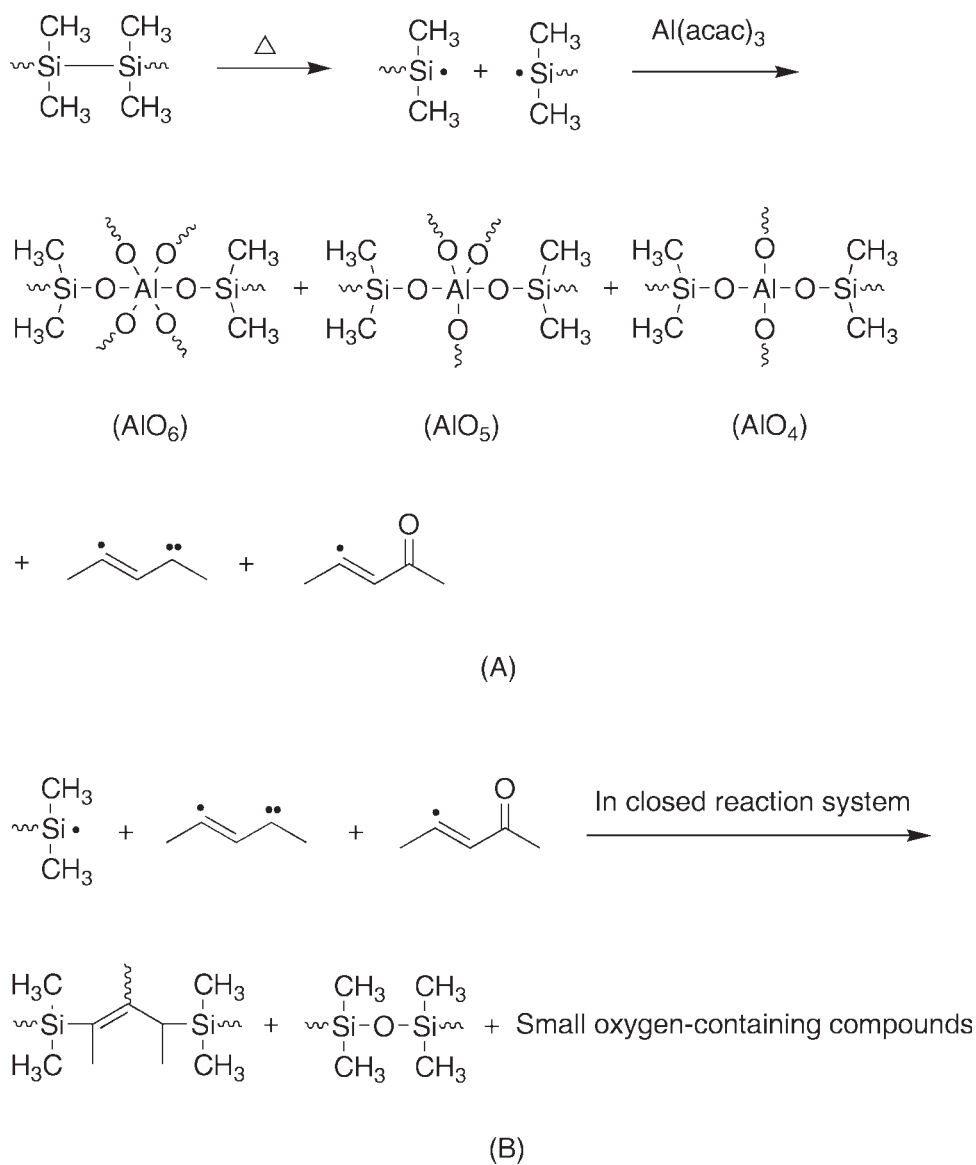


Figure 5  $^{27}\text{Al}$  MAS NMR spectra of (A) PACS-N and (B) PACS-M.



Scheme 2 Proposed mechanism for PACS formation.

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