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MOLECULAR WEIGHT DISTRIBUTION OF POLYCARBOSILANE AS A STARTING MATERIAL OF THE SILICON CARBIDE FIBER WITH HIGH TENSILE STRENGTH

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Polycarbosilane was fractionated by fractional solution. Relation between MW distribution and spinnability of polycarbosilane was obtained.

In the previous reports[1,2], a method of converting the polycarbosilane fibers into the continuous, high tensile strength β-SiC fibers was described. The mechanical behavior of β-SiC fiber, as well as the fiber making process, would be influenced by the properties of polycarbosilane. Because the spinnability of polycarbosilane differs from sample to sample, the molecular weight (MW) distribution of polymers used should be important.

Polycarbosilane was produced in the authors' laboratory by heating 250 grams of polysilane in an argon-filled autoclave at a temperature of 450°C for 14 hours[1]. The products in the autoclave were then dissolved in a suitable quantity of n-hexane and filtered. To obtain the solid polycarbosilane, n-hexane was distilled off in a water jet pump vacuum and then dried by heating up to 200°C in vacuum.

For fractionation, about 10 grams of powdered polycarbosilane was dissolved in 10 ml of n-hexane. The solution was then divided into soluble and precipitate parts by adding 60 ml of acetone as the non-solvent. The precipitate was successively fractionated into several fractions in the same manner.

Except the first acetone-soluble portion, each fraction was dried and dissolved in benzene to a concentration of about 2 mg/g, and the average MW was measured by a Hitachi 117 vapour pressure osmometer.

The average MW of the first acetone-soluble polycarbosilane (Mn_1) is evaluated from equation (1):

$$\bar{M}n = \frac{\Sigma\, n_i Mn_i}{\Sigma\, n_i} \quad (i = 1, 2, \text{---}) \qquad (1)$$

where $\bar{M}n$ is the measured average MW of unfractionated polycarbosilane, and n_i and Mn_i ($i=2,3,\text{---}$) are the number of moles and the measured average MW of fractionated polycarbosilanes, respectively.

Three distribution curves are shown in Fig. The polycarbosilane does not contain molecules of average MW smaller than 240, which is the average MW of distillate obtained by vacuum drying .

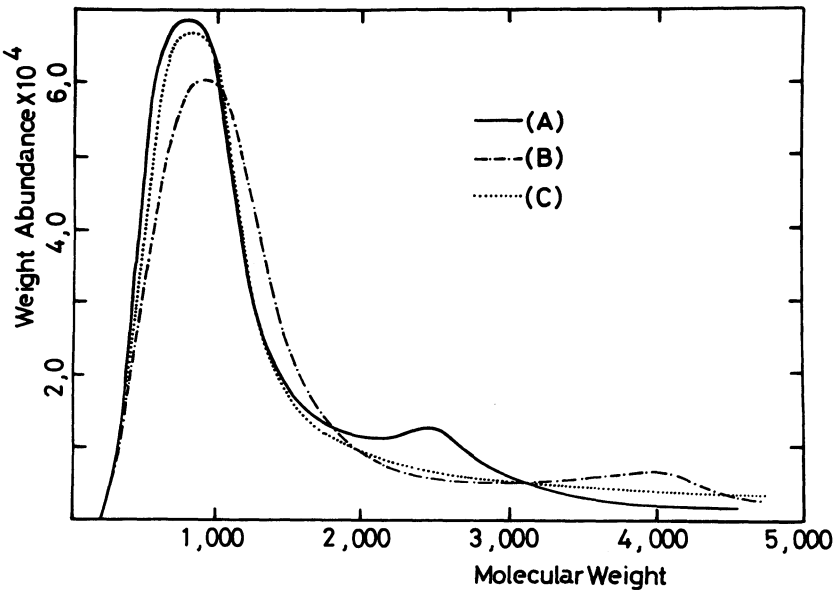

Fig. Molecular Weight Distribution Curves of Polycarbosilanes
(Average MW: (A)=1,086 (B)=1,226 (C)=1,199)

Spinnability of sample (A) and (B) is excellent. Tensile strength and Young's modulus of the subsequent β-SiC fiber are as high as 350 kg/mm^2 and 30 t/mm^2, respectively. Under the same spinning conditions, the spinnability of sample (C) is not so good as sample (A) and (B). This is attributed to the long tail of MW distribution of (C) at high molecular weight region. The results are tabulated below.

Table : Weight Percentage of High MW Polycarbosilane

Sample	A	B	C
MW>10,000	15	18	15
MW>25,000	unobtainable	unobtainable	10

The values by mathematical calculation are in agreement with the above. The "third moment about the mean of distribution", σ_3, is a measure of the skewness of distribution[3,4] as indicated by the equation:

$$\sigma_3 = \nu_3 - 3\nu_1\nu_2 + 2\nu_1^3 \qquad (2)$$

where $\nu_j = \frac{\Sigma\, n_i Mn_i^j}{\Sigma\, n_i}$ (j=1,2,3,---), the "first, second, third, --- moments of the distribution about zero".

The σ_3 values for sample (A), (B), and (C) are calculated to be 0.86×10^{10}, 1.49×10^{10}, and 6.73×10^{10}, respectively. The highest value in (C) is thus self-explanatory.

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