

Effects of Poly(vinyl alcohol) Suspension Medium on Critical Current Density of $\text{Ba}_2\text{Y}_1\text{Cu}_3$ Oxide Superconducting Filaments Produced by Suspension Spinning Method

TOMOKO GOTO* and KEISAKU YAMADA

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

SYNOPSIS

Superconducting $\text{Ba}_2\text{Y}_1\text{Cu}_3$ oxide filament was produced by means of the suspension spinning method. The effects of poly(vinyl alcohol) (PVA) suspension medium on structure and critical current density (J_c) of the filament sintered were explored with PVA of various degrees of polymerization (DP) in dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMTA) and the mixed solution of DMSO and HMTA (1 : 1). Although the PVA was removed as a volatile component by heating treatment of the filament, the dispersion behavior of the oxide powder in the filament was dependent on the suspension medium, hence the microstructure and superconducting properties of the filament obtained was affected by the suspension medium. The filament spun through the mixed solution of DMSO and HMTA had a high J_c of 77 K more than 100 A/cm^2 at the wide range of DP and powder content. The crystal grains of the oxide in the sintered filament grew finer with increasing the DP of PVA. On the other hand, the J_c of the filament produced by pure solution of DMSO and HMTA was not detected at DP of 3000 and 2450, respectively, due to the influence of entanglement of the molecular chains of PVA.

INTRODUCTION

The discovery of the high T_c oxide superconductor with T_c exceeding the liquid-nitrogen temperature promised wide application in future technology.¹⁻⁴ However, such oxide superconductors are usually brittle and difficult to fabricate into tapes or wires that are useful in large scale engineering applications such as superconducting magnets, power transmission lines, etc. A powder metallurgy technique is usually applied to fabricate the high T_c oxide superconducting into wires. Its application for superconducting magnets is also hindered by the weak-link problem in the sintered materials, which is typified by very low transport critical current densities and their severe degradation in weak magnetic field.

We have studied the preparation of the high T_c oxide superconducting long filament using a suspension spinning method.⁵⁻⁹ The oxide powder was suspended in a PVA solution and the viscous sus-

pension was extruded as a filament into a precipitating medium and coiled on a winding drum. The obtained filament was heated to remove the volatile component and to generate the superconducting phase. It is important in this technique to enhance the densification of the oxide in the filament and to form fewer and cleaner grain boundaries, reducing the Josephson junction "weak link" effect. The PVA suspension medium will play an important role in the dispersion of the oxide in the spinning dope and coagulation of the oxide through the precipitating medium. The present article deals with the effects of PVA suspension medium on the structure and J_c of the filament obtained.

EXPERIMENTAL

Suspension Spinning

A fine mixed powder with a nominal composition of $\text{Ba}_2\text{Y}_1\text{Cu}_3\text{O}_x$ was prepared by coprecipitating the carbonates of Ba, Y, and Cu. The powder was calcinated at 1123 K for 7.2 ks and the particle size of

* To whom correspondence should be addressed.

the heated powder was up to 200 nm. The powder was suspended in PVA solution. The suspension dope was extruded as a filament into a precipitating medium of methyl alcohol and coiled on a winding drum. The as-drawn filament was sintered at 1253 K for 300 s in oxygen gas flow, followed by furnace cooling at a cooling rate of 100 K/h. It is well known that the superconducting perovskite phase breaks up in aqueous solution. Then the effects of PVA nonaqueous suspension medium on structure and J_c of the filament sintered were explored with PVA in DMSO, HMTA, and the mixed solution of DMSO and HMTA (1 : 1). PVA with various degrees of polymerization (DP) was kindly supplied from Kuraray Co. Ltd. The molecular characteristics of the PVA used in this study are listed in Table I. The viscosity of the spinning dope, ranging from tens to several thousand poise, was controlled by changing the concentration of the PVA solution.

Physical Properties

The resistivity of the filament heated was measured by a standard four-probe method. A silver paint was used to contact Pt electrode of 70 μm in diameter. The temperature of the specimen was measured using a calibrated, chromel-gold + 0.07% iron thermocouple. The transport J_c measurement was performed at 77 K, 0 field with criterion of 1 $\mu\text{V}/\text{cm}$. The tensile strength of the as-drawn filament was measured by an Instron-type tensile testing machine. The microstructure of the filament was examined with scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Superconducting $\text{Ba}_2\text{Y}_1\text{Cu}_3$ oxide long filaments with 200 μm in diameter were produced from various PVA suspension media and the J_c of the filaments sintered was measured. The effect of the PVA suspension medium on J_c of the filament was explored with PVA of various DP in DMSO, HMTA, and the mixed solution of DMSO and HMTA (1 : 1).

Figures 1, 2, and 3 show the effect of DP of PVA on the J_c at 77 K of the filaments spun from the suspension solution of DMSO, HMTA, and the mixed solution of DMSO + HMTA, respectively. A spinning was not performed by using the PVA with low DP of 550. On this case a filament was made by lining the dope along the long length direction of the precipitating bath, as if the oxide line was painted in the precipitating medium. The J_c of the filament spun from pure solution abruptly dropped

Table I Molecular Characteristics of Poly(vinyl alcohol)

Sample	DP	Saponification Degree
1	550	98.5
2	1500–1800	min. 98.0
3	2450	98.5
4	3000	99.9
5	4700	99.9
6	8800	99.8
7	12,100	99.9
8	16,000	99.9
9	16,900	99.0

Sample 2 was a standard reagent and the other samples were supplied from Kuraray Co. Ltd.

at DP ranging from 2450 to 3000 and was not detected at DP = 2450 in DMSO and DP = 3000 in HMTA respectively. On the other hand, high J_c of more than 100 A/cm^2 was observed for the filament spun from PVA with a wide range of DP in the mixed solution of DMSO and HMTA. These are explained as follows: There will be a rheological entanglement value of molecular weight (M_c) in concentrated PVA solution. On the suspension spinning, the polymer with DP near M_c will entangle each other and will play the role of spinnability for the long filament but will have no effect for the dispersion of the oxide powder by way of prevention of the mobility of a molecular chain. Oyanagi and Matsmoto made viscosity measurements on concentrated aqueous solutions of PVA samples, where relative viscosities (η) of PVA solutions were plotted against the molecular weight (M) of the polymer. It was evident that the proportionality of η to $M^{3.4}$ was an often observed feature, particularly when high polymer concentrations and high molecular weights were involved and M_c (starting point of the proportionality) was estimated from the curves at DP = 4000 and 3000 for the dilute solution of 0.04 wt % and 0.06 wt %, respectively.¹⁰ These values are considered to be reasonable for the present spinning condition. M_c in HMTA is slightly higher than that in DMSO because of the dilute spinning concentration of HMTA. M_c for the mixed solution of DMSO and HMTA will be between 2450 and 3000 and the abnormal behavior was not detected experimentally.

The tensile strength of the filament without sintering, which was spun by using PVA with various DP in the mixed solution of DMSO and HMTA, was measured and the results are shown in Figure 4. A low tensile strength and a high elongation were measured for the filament without sintering except

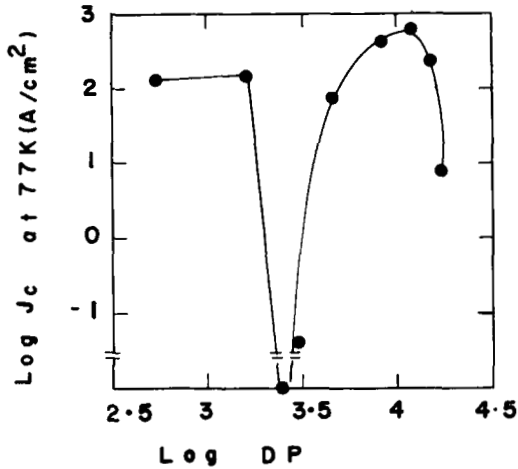


Figure 1 Relation between critical current density at 77 K and degree of polymerization of PVA from the suspension solution of DMSO.

for the filament spun by PVA with a low DP of 550, as compared to the sintered filament, which had a high tensile strength of more than 20 MPa and low elongation of 0.8%. The maximum tensile strength with minimum elongation was observed at a DP of 3000; the tensile strength decreased and elongation increased with increasing the DP more than 3000. The entanglement of the molecular chains of PVA will occur near the Mc point and will prevent the mobility of the molecular chain, resulting in brittleness of the filament and then the flexibility will increase with increasing the length of the molecular chain.

The surface and cross-section of the filament produced by this method was observed by SEM. The

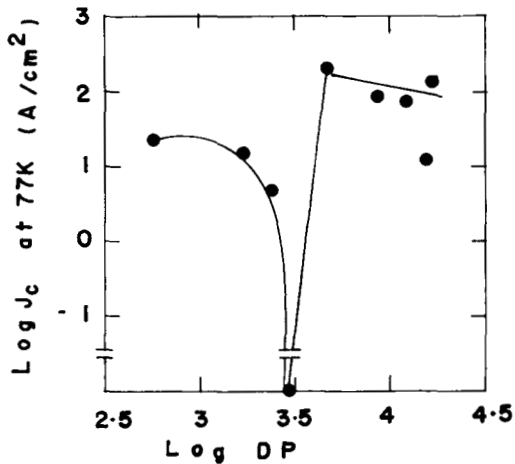


Figure 2 Relation between critical current density at 77 K and degree of polymerization of PVA from the suspension solution of HMTA.

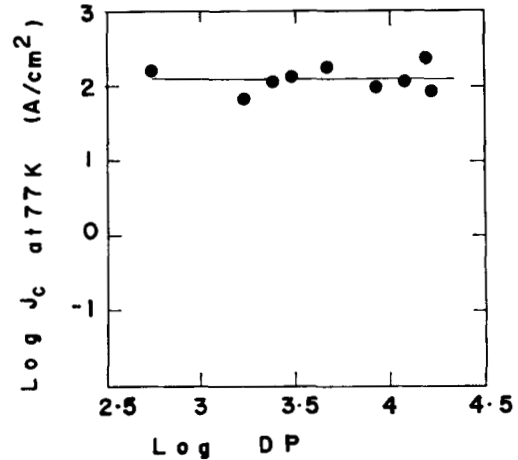


Figure 3 Relation between critical current density at 77 K and degree of polymerization of PVA from the mixed solution of DMSO and HMTA.

oxide powder was knit together by heat treatment and was packed densely in the filament on the observation of the cross-section. The structure of the surface of the filament spun by the mixed solution of DMSO and HMTA varied with DP, as shown in Figure 5. The oxide powder was drawn up the blade type grains with a grain size of $4 \mu\text{m} \times 6 \mu\text{m} \times 1 \mu\text{m}$ for the filament spun by using PVA with a DP of 4700, exhibiting the J_c at 77 K of 194 A/cm^2 . The blade became smaller to the grain size of up to $2 \mu\text{m} \times 3 \mu\text{m} \times 1 \mu\text{m}$ by using a DP of 12,100 ($J_c = 113 \text{ A/cm}^2$) and finally turned to the particles with a diameter of more than $0.4 \mu\text{m}$ from DP of 16,000

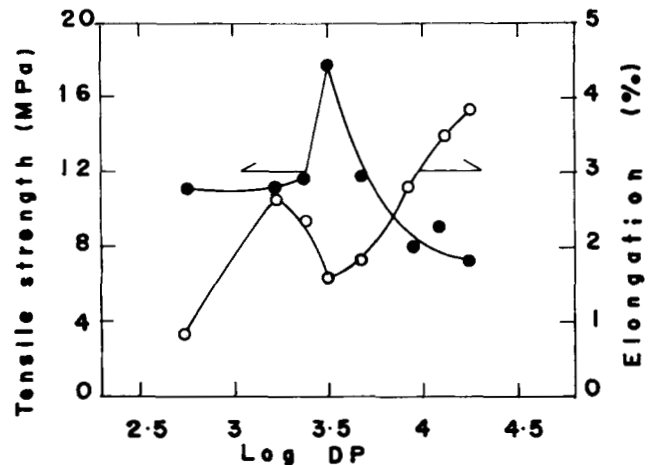


Figure 4 Tensile strength and elongation of the filament without sintering, which was spun by using PVA with various DP in the mixed solution of DMSO and HMTA. Closed circles indicate tensile strength and open circles indicate elongation.

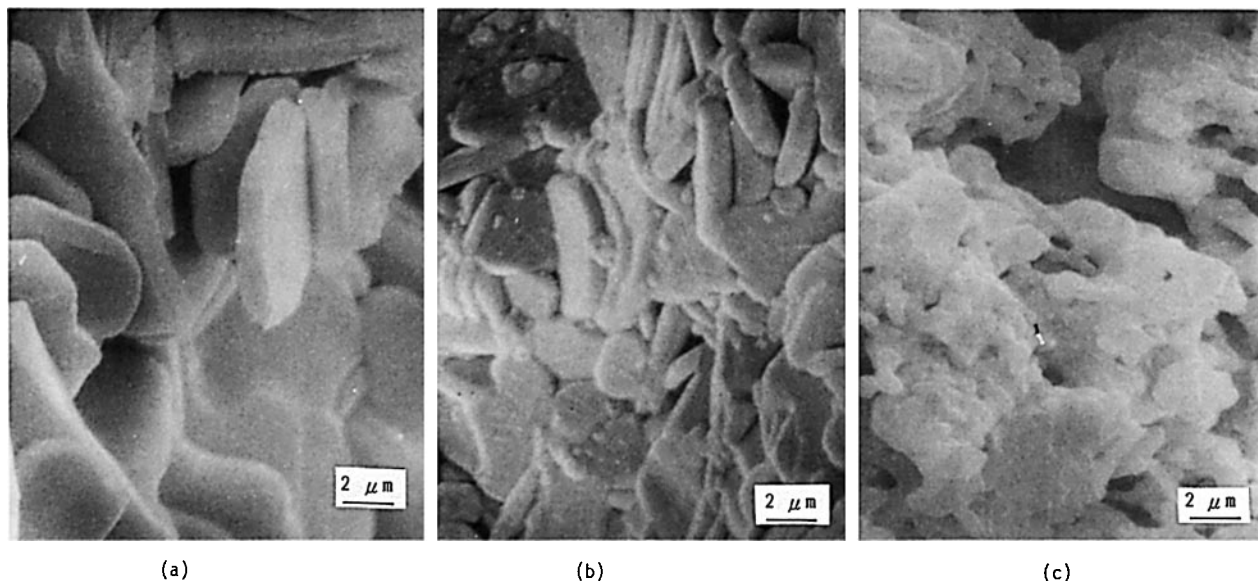


Figure 5 Surface structure of the filament spun by using PVA with various DP in the mixed solution of DMSO and HMTA. (a) DP = 4700, (b) DP = 12100, and (c) DP = 16000.

($J_c = 254 \text{ A/cm}^2$). The J_c of the filament spun by using high DP of 16,000 was slightly high. According to the increase of the molecular chain length of PVA, the flexibility of the chain will increase, the formation of micelles is supposed to be enhanced under special macromolecule fields, and the oxide powders will be dispersed more finely and more uniformly. The J_c of the filaments was dependent on the oxide powder content. The J_c of the filaments spun through various powder contents of the spinning dope of PVA with DP of 12,100 in DMSO, HMTA, and in the mixed solution of DMSO and HMTA is shown in Figures 6, 7, and 8, respectively. A maximum J_c of the filament spun in DMSO, HMTA, and the mixed solution was measured at the oxide content of 95, 93 and 96 wt %, respectively. The critical molecular concentration (cmc) of PVA needed to play the dispersant in the spinning dope and coagulator of the oxide through the precipitating medium is suggested to be at ranging from 7 wt % to 4 wt %. On the other hand, the densification of the filament will increase with increasing the oxide content. The J_c curve of Figures 6, 7, and 8 can be explained by overlapping the effect of oxide density of the filament and the cmc of PVA. As the polarity of the solvent is considered to be related to the cmc, the maximum values varied with solution. It is known that PVA molecules in the aqueous spinning solution follow the general behavior of polar vinyl polymers and under particular circumstances the effect of hydrogen bonding is observed.¹¹

The J_c of the filaments spun through the mixed solution of DMSO and HMTA was higher than that for the pure solution and showed more than 100 A/cm^2 at the wide range of concentration because of the multiplied effect of the each solution. Thus the filament spun through the mixed PVA solution of DMSO and HMTA had high J_c at the wide range of DP of PVA and content of the oxide.

As the characteristics of the polymer solution is considered to contribute to these results, the vis-

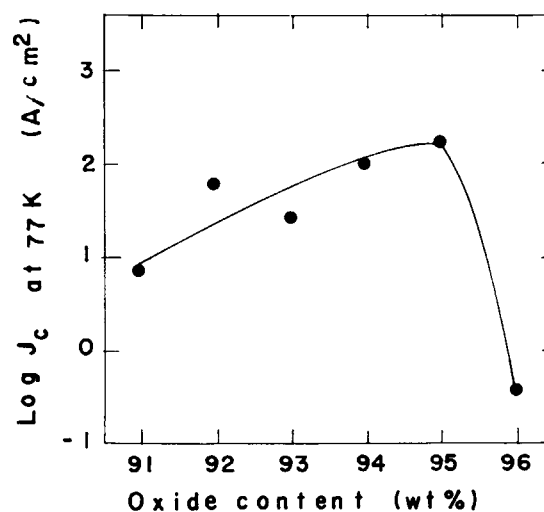


Figure 6 Relation between critical current density at 77 K and oxide powder contents of the filament spun from DMSO.

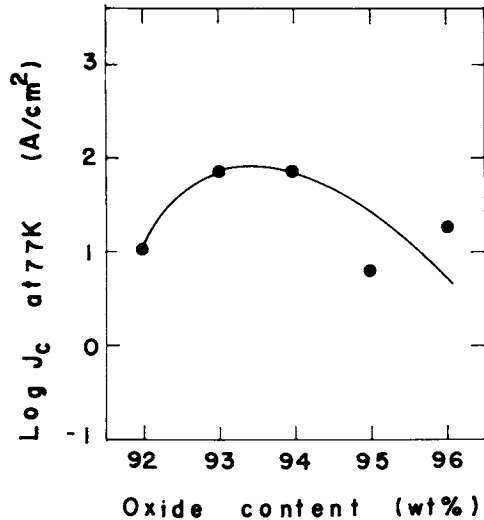


Figure 7 Relation between critical current density at 77 K and oxide powder contents of the filament spun from HMTA.

cosity measurements of PVA solution at 303 K were investigated to clarify the conformation of the polymer in each solution. According to the relation between intrinsic viscosity $[\eta]$ and molecular weight M ,

$$[\eta] = KM^\alpha \quad (1)$$

where K is a constant for a homologous series of polymers of a given molecular structure and α is an exponent that varies between 0.5 and 0.8 for polymer solution. The theoretical situation is as follows: for random-coil molecules in very poor solvents (θ solvent), α is 0.5; for high molecular weight random coils in good solvents, α is about 0.8. Figure 9 shows the relation between $\log [\eta]$ and M in a PVA solution of DMSO, HMTA, and the mixed DMSO and HMTA. The α values for DMSO, HMTA, and the mixed solution of DMSO and HMTA are estimated to be 0.56, 0.71, and 0.64, respectively. Although these results show the information of PVA dilute solution, the conformation of polymer in concentrated solution may be estimated by using parameter α in eq. (1).¹²

DMSO was very poor solvent for PVA, while HMTA was a good solvent. Hence the distance between the ends of the molecular chains of PVA in the mixed solution of HMTA and DMSO will be larger than that for DMSO and the molecule in the mixed solution can disperse the oxide more uniformly than that for the DMSO solution. Although

HMTA is a good solvent for PVA, the polarity was not so suitable for the oxide powder as shown in Figure 7. Moreover, the spinning operation from HMTA was difficult due to the high viscosity of the solution and poor coagulation in the precipitating medium of methyl alcohol.

CONCLUSIONS

The effects of PVA suspension medium on the structure and J_c of the $Ba_2Y_1Cu_3$ oxide filament produced by suspension spinning was studied. The superconducting long filaments, 200 μm in diameter, were produced from various PVA suspension media by using PVA with various DP in DMSO, HMTA, and the mixed solution of DMSO and HMTA; the J_c of the sintered filament was measured. High J_c at 77 K more than 100 A/cm^2 was observed for the filament spun in the mixed solution at the wide range of DP and powder content.

However, the J_c was not detected for the pure solution of DMSO and HMTA at DP of about 3000 due to the effect of the entanglement value of molecular weight. The structure of the surface of the filament spun in the mixed solution of DMSO and HMTA varied with DP of PVA and the grain size of the oxide decreased with increasing the DP more than 3000. DMSO was a poor solvent for PVA and HMTA was a good solvent. The polarity of the PVA solution of HMTA was not suitable for the oxide and the spinning operation was difficult. The PVA

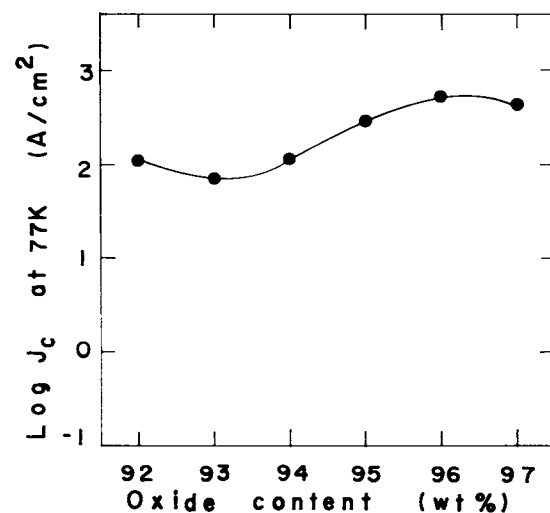


Figure 8 Relation between critical current density at 77 K and oxide powder contents of the filament spun from the mixed solution of DMSO and HMTA.

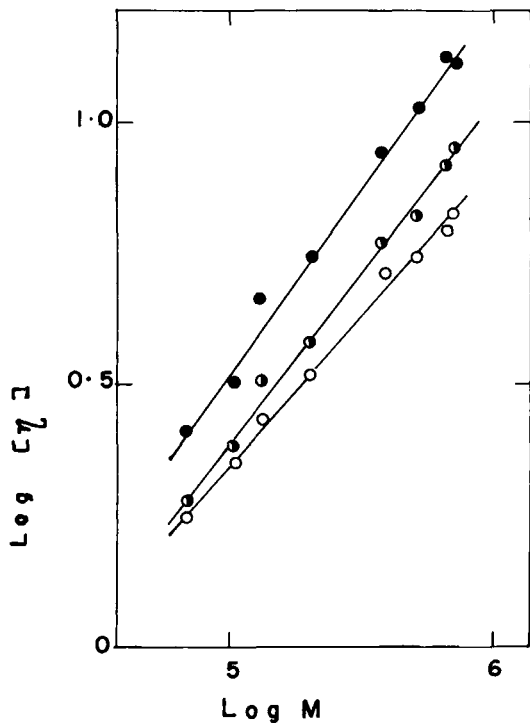


Figure 9 Intrinsic viscosity as a function of molecular weight of PVA. The points represent measurements in DMSO (○), HMTA (●) and the mixed solution of DMSO and HMTA (◐).

suspension medium in the mixed solution of DMSO and HMTA was effective for the suspension spinning of the $\text{Ba}_2\text{Y}_1\text{Cu}_3$ oxide by multiplying the effect

of each solution. The medium was able to control the structure of the sintered filament by changing the DP of PVA.

REFERENCES

1. J. Bednorz and A. K. Muller, *Z. Phys. B.*, **64**, 189 (1986).
2. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.*, **58**, 908 (1987).
3. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys.*, **27**, L209 (1988).
4. Z. Z. Sheng and A. M. Hermann, *Nature*, **332**, 10 (1988).
5. T. Goto, I. Horiba, M. Kada, and M. Tsujihara, *Jpn. J. Appl. Phys.*, **26**(3), 1211 (1987).
6. T. Goto and M. Kada, *Jpn. J. Appl. Phys.*, **26**, L1527 (1987).
7. T. Goto, *Jpn. J. Appl. Phys.*, **27**, L680 (1988).
8. T. Goto and K. Takeuchi, *Jpn. J. Appl. Phys.*, **27**, L1845 (1988).
9. T. Goto and M. Kada, *J. Mater. Res.*, **3**, 1297 (1988).
10. Y. Oyanagi and M. Matsumoto, *J. Colloid Sci.*, **17**, 426 (1962).
11. T. Osugi, *Man-Made Fibers, Vol. III*, H. F. Mark, S. M. Atlas, and E. Cernia, eds., Interscience, New York, 1968, p. 245.
12. S. Onogi, T. Masuda, N. Miyana, and Y. Kimura, *J. Polymer Sci.*, **A-2**(5), 899 (1967).

Received June 6, 1989

Accepted February 22, 1991