

ELECTRICAL CONDUCTIVITY OF IODINE DOPED POLY(PHTHALOCYANINATOSILOXANE) / PPTA BLEND FIBERS

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ABSTRACT

Poly(phthalocyaninosiloxane), $[\text{Si}(\text{Pc})\text{O}]_n$, with the number average degree of polymerization of about 130 was prepared by heating its monomer $\text{Si}(\text{Pc})(\text{OH})_2$, in solid state at 420°C for 42 hrs at 10^{-3} torr dynamic vacuum. The $[\text{Si}(\text{Pc})\text{O}]_n$ powder was iodine doped with I_2 -benzene solution for 48 hrs. Pure iodine doped poly(phthalocyaninosiloxane), $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_2\}_n$, fibers and $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_2\}_n$ /poly(p-phenylene terephthalamide) blend fibers were wet-spun with dry nitrogen-sealed Teflon lined device. D.C. electrical conductivity of the fibers was measured by the four-probe method with an automated charge transport measurement system from 80K to room temperature. It was found that the dependence of conductivity, σ , on temperature, T , could fit a group of thermal fluctuation-induced tunnelling (TFIT) equations, and that the dependence of conductivity on volume fraction, ϕ , of the iodine doped $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_2\}_n$ could fit a group of modified percolation equations. A three-dimensional composite plot of $\sigma^{-1}/T-\phi$ shows that these two groups of equations match each other quite well. It has been pointed out that for the blend fibers their composition is the most important factor for both mechanical and electrical properties.

INTRODUCTION

As an electronic conductive polymer, iodine-doped poly(phthalocyaninosiloxane), $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_2\}_n$, has not only high conductivity, which can reach an order of $10^0 (\Omega^{-1}\text{cm}^{-1})^{[1]}$, but also has good air, water and thermal stability, and high processability^[2]. Since poly(phthalocyaninosiloxane), $[\text{Si}(\text{Pc})\text{O}]_n$, is a kind of one-dimensional conductive polymer^[1,3], it is a good try to spin it into a fiber^[4] which has a superior dimension in size. If the electronic conductive direction is coincident with the fiber axis, the conductivity along the fiber axis will increase. Spinning into fiber is also a sort of first step to practical application of this electronic conductive polymer.

The pure $[\text{Si}(\text{Pc})\text{O}]_n$ fiber, however, is brittle. It seems to be a good idea to make $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_2\}_n$ fiber blending with poly(p-phenylene terephthalamide), PPTA, to improve its mechanical property^[4]. In this aspect of research, nothing has been done before except the preliminary report given by Inabe et al.^[4]. Their experimental data of temperature dependence of conductivity for the blend fibers fit the equation as follows:

$$\sigma = \sigma_0 \exp[-T_1/(T + T_0)] \quad (1)$$

They suggested a transport mechanism involving thermal fluctuation-induced tunnelling (TFIT) between conductive domains in an inhomogeneous medium. It has not been studied about the

composition dependence of conductivity for $\{[Si(Pc)O]I_y\}_n$ /PPTA blend fibers. They also reported that pure Kevlar fibers spun by the same procedure absorb minimal iodine and are electrical insulators. It means that in $\{[Si(Pc)O]I_y\}_n$ /PPTA blend fibers, there are two species: conductive $\{[Si(Pc)O]I_y\}_n$ and insulating PPTA. It has been found that a percolation model^[5] can be used to explain the composition dependence of conductivity of such kind of mixed system. For a water-oil microemulsion system^[6], it was found that there are two transition points on the experimental curves of conductivity vs. water concentration: the percolation threshold at low water concentration region and the inversion concentration at high water concentration region. Beyond the inversion concentration, the curves are bent upwards since the water becomes a continuous phase from a dispersed one.

In the present work, we try to know whether both percolation effect and TFIT mechanism can match the same observed results of $\{[Si(Pc)O]I_y\}_n$ /PPTA blend fibers.

EXPERIMENTAL

Original samples

$[Si(Pc)O]_n$ sample used here was prepared by heating its monomer $Si(Pc)(OH)_2$ in solid state at $420^\circ C$ for 42 hrs. at 10^{-3} torr dynamic vacuum^[3]. Tritium labelling studies^[1] have determined that the number average degree of polymerization, $\bar{n}$, is about 130. PPTA was kindly offered by Du Pont Company.

Fiber samples preparation

Pure $\{[Si(Pc)O]I_y\}_n$ fibers and $\{[Si(Pc)O]I_y\}_n$ /PPTA blend fibers were wet-spun with dry nitrogen-sealed Teflon lined device^[4]. The diameter, D , and length, L , of the spinneret orifice used here were 0.33 mm and 5 mm, respectively. Processing of fiber spinning is quite similar to the previous study^[4]. $[Si(Pc)O]_n$ powder was iodine doped with I_2 -benzene solution for 48 hours before using it to make fibers. Around 15 weight % concentrated spinning dope was prepared in trifluoromethane-sulphonic acid, CF_3SO_3H , at $80^\circ C$ in dry nitrogen atmosphere, under vigorous stirring. After about 20 hrs. rest and deaeration, it was spun into a room temperature water bath for coagulating. Then, it was washed with water at room temperature for about 20 hrs., dried in air.

Composition of blend fibers was determined with quantitative microanalyses by Galbraith Laboratories, Inc, Knoxville, TN; these results indicated that relative amounts of the two polymers mixed in the spinning solution were the same as what was obtained in the finished fibers.

Conductivity measurement

D.C. electrical conductivity of iodine doped pure $\{[Si(Pc)O]I_y\}_n$ and $\{[Si(Pc)O]I_y\}_n$ /PPTA fibers were measured by the four-probe method with an automated charge transport measurement system (1). The temperature range of conductivity measuring is from room temperature down to 80K. Sample fibers were mounted on a glass cover-slip which was affixed to a copper heat sink by vacuum grease. Electrical connections were accomplished with 0.025 mm gold wires in diameter across the fiber surface and further joined with conductive gold paste. The agreement between conductivity values was typically within $\pm 2\%$ of the mean.

RESULTS

A family of temperature dependence of conductivity of $\{[Si(Pc)O]I_y\}_n$ /PPTA blend fibers is given in Fig.1. The top curve shows the conductivity of the pure $\{[Si(Pc)O]I_y\}_n$ fiber vs. $10^3/T$, the

bottom one is that of 20 volume % {[Si(Pc)O]I_y]_n blend fiber. Between them are those of 90, 75, 66.7, 60, 50, 40 volume % curves, respectively. All of the curves show that their conductivities almost exponentially increase with temperature.

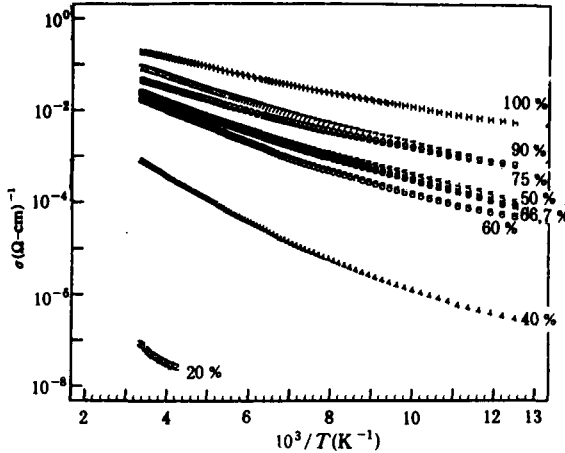


Fig.1 A family of experimental temperature dependence of conductivity of {[Si(Pc)O]I_y]_n/PPTA blend fibers.
(H:100 volume % {[Si(Pc)O]I_y]_n, 9: 90%, 7: 75%, *: 66.7%, 6: 60%, 5: 50%, 4: 40%, 2: 20%)

For the volume fraction dependence of conductivity of {[Si(Pc)O]I_y]_n/PPTA blend fibers, on the basis of linear regression treatment, it was found that a modified percolation model could fit the observed data quite well. The data at 300K, 200K, 150K, 130K, 110K, 94K, and 80K were chosen to be treated. The classical percolation model^[6] is

$$\sigma = \sigma_0(\varphi - \varphi_c)^t \quad \text{when } \varphi > \varphi_c \quad (2)$$

where σ is conductivity, σ_0 is a constant, φ is the volume fraction of conductive species, φ_c is the percolation limit below which the conductivity falls to a very small value, and t is a percolation exponent, for a three-dimensional continuous random system, it falls in the range of 1.3—1.7.

In order to fit the observed data, a small modification of percolation model was used here as follows:

$$\begin{aligned} \sigma(T, \varphi) &= \sigma_0(T)(\varphi - \varphi_c)^t & \text{for } \varphi_c < \varphi < \varphi_i \\ \sigma(T, \varphi) &= \sigma_0(T) & \varphi = 1 \end{aligned} \quad (3)$$

where φ_i is the inversion volume fraction beyond which the conductivity increases more steeply with {[Si(Pc)O]I_y]_n fraction.

Another hypothesis we used to treat our data is that for {[Si(Pc)O]I_y]_n/PPTA blend fiber system the percolation exponent, t , should be the same value. Based on these two hypotheses, we obtained the following group of equations and their correlation coefficients, R :

$$\begin{aligned} \sigma(300, \varphi) &= 1.56 \times 10^{-1}(\varphi - 0.198)^{2.364} & R &= 0.99 \\ \sigma(200, \varphi) &= 1.38 \times 10^{-1}(\varphi - 0.352)^{2.359} & R &= 0.98 \\ \sigma(150, \varphi) &= 5.44 \times 10^{-2}(\varphi - 0.369)^{2.361} & R &= 0.97 \\ \sigma(130, \varphi) &= 3.16 \times 10^{-2}(\varphi - 0.375)^{2.345} & R &= 0.97 \\ \sigma(110, \varphi) &= 1.70 \times 10^{-2}(\varphi - 0.380)^{2.347} & R &= 0.97 \\ \sigma(94, \varphi) &= 8.79 \times 10^{-3}(\varphi - 0.383)^{2.357} & R &= 0.97 \\ \sigma(80, \varphi) &= 4.42 \times 10^{-3}(\varphi - 0.385)^{2.382} & R &= 0.97 \end{aligned} \quad (4)$$

The above group of equations exhibits that when the exponents close to 2.36, all of the correlation coefficients are larger than 0.96. According to our second hypothesis, the above equations may be arranged into the following equations using a uniform exponent, $t = 2.36$.

$$\begin{aligned}
 \sigma(300, \varphi) &= 1.56 \times 10^{-1}(\varphi - 0.198)^{2.36} \\
 \sigma(200, \varphi) &= 1.38 \times 10^{-1}(\varphi - 0.352)^{2.36} \\
 \sigma(150, \varphi) &= 5.44 \times 10^{-2}(\varphi - 0.369)^{2.36} \\
 \sigma(130, \varphi) &= 3.16 \times 10^{-2}(\varphi - 0.375)^{2.36} \\
 \sigma(110, \varphi) &= 1.70 \times 10^{-2}(\varphi - 0.380)^{2.36} \\
 \sigma(94, \varphi) &= 8.79 \times 10^{-3}(\varphi - 0.383)^{2.36} \\
 \sigma(80, \varphi) &= 4.42 \times 10^{-3}(\varphi - 0.385)^{2.36}
 \end{aligned} \quad (5)$$

From these equations, we can obtain a group of calculated composition dependent conductivity curves, as shown in Fig.2. Below 90% of $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ volume fraction, the solid lines are based on the calculated data; beyond 90%, the curves bend upwards, using a dashed line to connect with the pure $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ data. They fit the experimental data quite well. Their percolation limits are pretty closed except the one at 300K.

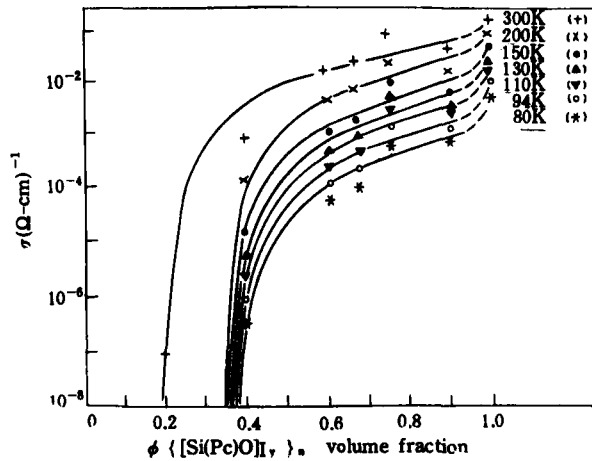


Fig.2 A family of calculated volume fraction dependent conductivity curves of $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ /PPTA blend fibers from equation group (5).

As we have mentioned, the temperature dependence of observed conductivity data of $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ /PPTA blend fibers fits a TFIT mechanism. Now, in order to confirm whether the modified percolation model is in a good agreement with original data or not, and to know whether both percolation model and TFIT mechanism can match the same experimental results, using linear regression, we treated the calculated data from equation group (5) to go back to the temperature dependence of conductivity, and we got the following group of TFIT conductivity equations, as well as their correlation coefficients:

$$\begin{aligned}
 \sigma(T, 100\%) &= 8.19 \times 10^{-1} e^{-419/T} & R &= -0.99 \\
 \sigma(T, 90\%) &= 5.91 \times 10^{-1} e^{-677/(T+24)} & R &= -0.99 \\
 \sigma(T, 75\%) &= 4.90 \times 10^{-1} e^{-846/(T+38.9)} & R &= -0.99(9) \\
 \sigma(T, 66.7\%) &= 5.04 \times 10^{-1} e^{-1038/(T+54.1)} & R &= -0.99(9) \\
 \sigma(T, 60\%) &= 6.41 \times 10^{-1} e^{-1331/(T+74.6)} & R &= -0.99(99) \\
 \sigma(T, 40\%) &= 3.20 e^{-2873/(T+90)} & R &= -0.99
 \end{aligned} \quad (6)$$

Also, the calculated curves from these equations were drawn out in Fig.3. Both top and bottom curves are in accord with the experimental data which are marked with "+" or "x", respectively. It is, therefore, confirmed that the modified percolation model is suited to the volume fraction dependence of conductivity for $\{[\text{Si}(\text{Pc})\text{O}]_n\}$ /PPTA blend fiber system. Another benefit of this treatment is that the other curves between the top and bottom ones are rearranged in a reasonable order.

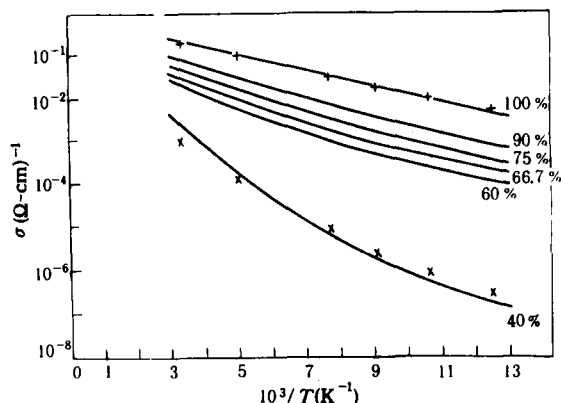


Fig.3 A family of calculated temperature dependent conductivity curves of $\{[\text{Si}(\text{Pc})\text{O}]_n\}$ /PPTA blend fibers from equation group (6)

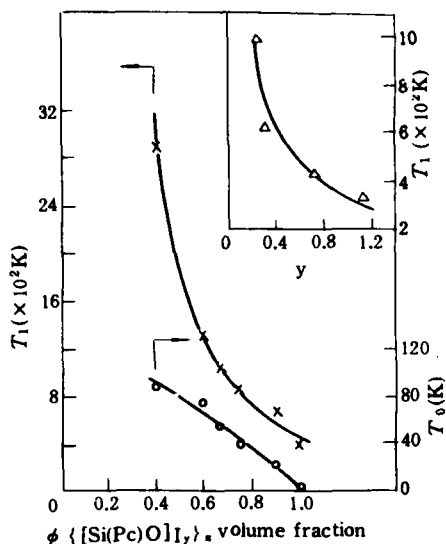


Fig.4 $\{[\text{Si}(\text{Pc})\text{O}]_n\}$ fraction dependences of two parameters, T_1 and T_0 , in thermal fluctuation-induced tunnelling equations for $\{[\text{Si}(\text{Pc})\text{O}]_n\}$ /PPTA blend fibers. The solid lines were plotted according to the equations of (7) and (8), $T_1 = 440/\varphi^{2.1}$ and $T_0 = 120(1.02 - \varphi^{1.5})$. The data marked with "x" or "o" were calculated from equation group (6).

Inset: A plot of T_1 vs. y , iodine doping level for pure $\{[\text{Si}(\text{Pc})\text{O}]_n\}$ powder compressed samples. The solid line was plotted according to the equation of (9), $T_1 = 330/y^{0.7}$. The data marked with "Δ" were quoted from Ref.[1].

From equation group (6), we found that both T_1 and T_0 were dependent on the $\{[Si(Pc)O]I_y\}_n$ volume fraction. Their relations can be expressed as follows:

$$T_1 = 440 / \varphi^{2.1} \quad (7)$$

$$T_0 = 120(1.02 - \varphi^{1.5}) \quad (8)$$

According to these equations, we plotted $T_1 - \varphi$ and $T_0 - \varphi$ curves with solid lines in Fig.4, including the data calculated from equation group (6) with the symbols "X" or "O", respectively. The $T_1 - \varphi$ curve shows that the effective barrier activation energy, T_1 , drops down rapidly with the increase of φ , especially in the low $\{[Si(Pc)O]I_y\}_n$ fraction region. T_0 determines the low-temperature temperature-independent conductivity. The $T_0 - \varphi$ curve reveals that T_0 increases with the decrease of φ , that is, low-temperature temperature-independent conductivity increases with the decrease of φ .

Now, we combine two families of curves, $\sigma - \varphi$ and $\sigma - 10^3 / T$, into a three-dimensional composite plot (Fig.5). It shows very clearly how the conductivity changes with temperature and composition. Also, it shows that, at the crosspoints of two families of curves, the conductivity is pretty closed. It is, therefore, indicated that both the modified percolation equation group and the TFIT equation group used here are matched quite well for the $\{[Si(Pc)O]I_y\}_n$ / PPTA blend fiber system.

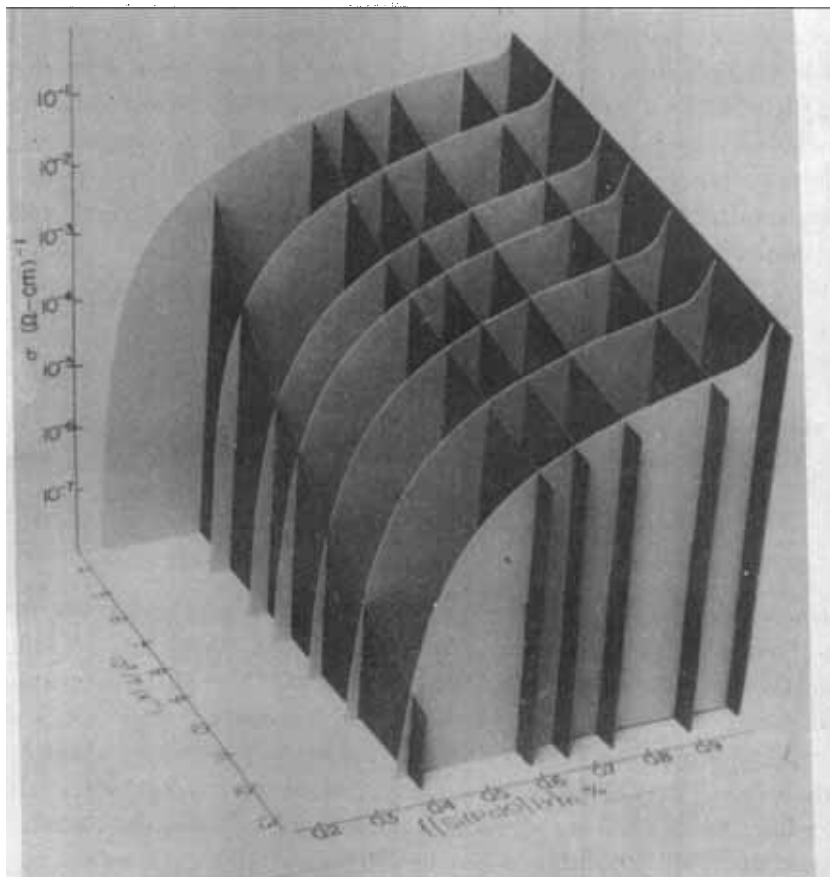


Fig.5 A 3-dimensional calculated composite plot of $\sigma - 10^3 / T - \varphi$ of $\{[Si(Pc)O]I_y\}_n$ / PPTA blend fibers from equation groups (5) and (6).

DISCUSSION

The $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n/\text{PPTA}$ blend fiber is a kind of polyphase system. In the blend fibers, PPTA tend to be a continuous phase since the solubility of PPTA in $\text{CF}_3\text{SO}_3\text{H}$ is higher than that of $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ and some other reasons. Only at very high $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ region it will be inverted, and $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ becomes a continuous phase. The two groups of conductivity equations match each other quite well and have a good agreement with the experimental data. It implies that they have expressed the main points of the conductive mechanism of the blend fibers.

In addition, since the blend fiber is a more complicated polyphase system, some of the parameters are in slight difference with the usual ones. Such as, the percolation exponent, t , could be 1.5^[5], 1.75^[7], or 2^[8] for site percolation from calculation for all $\varphi > \varphi_c$, respectively, and it could vary from 1.38 to 2.0 from experiments^[9]. For the $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n/\text{PPTA}$ blend fibers, we found that t is 2.36. It is somewhat larger than those data mentioned above. The fact that the composition dependent conductivity curves of the blend fibers bend upwards at the high $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fraction region means that the exponent, t , increases with $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fraction at that region. This may be due to the phase inversion of $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ from dispersed phase to a continuous one.

Another parameter, φ_c , is about 0.15 usually. In practice, however, there is a big discrepancy for this value from system to system. It could be as small as 0.07 for carbon black in wax^[10] and as large as 0.75 for Mo-SiO₂ system^[11]. Therefore, our data, round 0.2—0.4 for φ_c , is acceptable.

It has not been found in literature on the study of temperature dependence of φ_c . For $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n/\text{PPTA}$ blend fiber, we found that φ_c increases with the decrease of the temperature, but at low temperature, it is quite close. As we have pointed out, T_1 increases with the decrease of φ . Especially in the low $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fraction region T_1 changes rapidly. The tendency of changing here is similar to that for pure $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ powder compressed samples. For the sake of contrast, using the data in Ref.[1], we insetted a plot of T_1 vs. y , the dopant level, at the corner of Fig.5. The data marked "Δ" were quoted from Ref.[1], and the solid line was plotted based on the following equation:

$$T_1 = 330/y^{0.7} \quad (9)$$

This comparison indicated that the tendency of T_1 changing with φ is acceptable. Therefore, using equations (7) and (8), the exponential term in the TFIT equations can be expressed as follows:

$$\exp \left\{ - \frac{440}{\varphi^{2.1} [T + 120(1.02 - \varphi^{1.5})]} \right\} \quad (10)$$

If one wants to keep the value of this exponential term to a certain level, φ will decrease when T increases. From this angle, it seems that one could understand why φ_c decreases with T increasing.

From the above discussion, one could find that for the blend fibers, composition is the most important factor for determining both mechanical and conductive properties. Changing the $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fraction from 20% to 100%, the conductivity will change about 7 order at room temperature. Pure $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fiber has pretty good conductivity, but bad mechanical property. After blending with PPTA, it can be improved at the cost of decreasing the conductivity. The more it is blended with PPTA the better the mechanical property, but the lower the conductivity. We found that 75% $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n/25\%$ PPTA is a kind of good composition. In this case, the conductivity ratio between 75% blend fiber and 100% $\{[\text{Si}(\text{Pc})\text{O}]\text{I}_y\}_n$ fiber is as follows:

$$\sigma(T, 75\%) / \sigma(T, 100\%) = (0.75 - \varphi_c)^{2.36} \quad (11)$$

around room temperature, $\varphi_c = 0.2$, the ratio is 0.24; from $T = 200\text{K}$ down to 80K , $\varphi_c = 0.37$, the ratio is 0.1. This means that 75% $\{\text{Si}(\text{Pc})\text{O}[\text{I}_y]_n\}$ fiber reduces conductivity about one order of magnitude, but its strength is pretty good. It is obvious that in order to obtain a satisfactory blend fiber of $\{\text{Si}(\text{Pc})\text{O}[\text{I}_y]_n\}$ / PPTA with good mechanical quality and high electrical conductivity, the decisive step is choosing the proper composition.

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