

Polyphenyleneisoxazole 의 물리적 특성

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Physical Characteristics of Polyphenyleneisoxazole

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Abstract

A highly crystalline polyphenyleneisoxazole from the condensation reaction of terephthalohydroxamoyl chloride with 1,4-diethynylbenzene was consisted of smaller conjugation, which was demonstrated by the electronic spectra. The electric conductivity was decreased with elevating temperature. The correlation of electric conductivity with crystalline structure was studied.

Introduction

In a previous paper¹⁾, the author reported the physical properties of some polyphenyleneisoxazolines concerned with their crystallinities and electric conductivities. As has been reported,²⁾ a highly crystalline polyphenyleneisoxazole could be synthesized from the direct condensation reaction of terephthalohydroxamoyl chloride with 1,4-diethylbenzene in toluene. The stable free radicals were also included in this polymer³⁾. It therefore appeared of interest to investigate the physical properties of highly crystalline polyphenyleneisoxazole for elucidating the correlation between the polymer structure and physical characteristics in solid state. In the present paper, the author wish to describe physical characteristics of

polyphenyleneisoxazole, emphasizing on its electric property.

Experimental

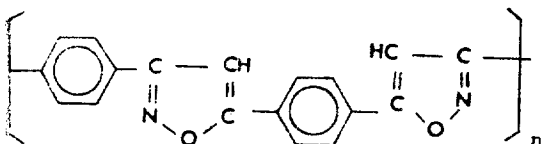
Polycondensation²⁾

Polyphenyleneisoxazole used was synthesized as follows.

An equivalent mole of terephthalohydroxamoyl chloride with 1,4-diethynylbenzene were refluxed in toluene until dehydrochlorination ceased. The polymer obtained was purified by extracting in hot methanol and characterized by the I. R and elementary analysis. Found N%=9.5. Calculated N%=9.5. $\nu_{\text{C}=\text{C}}$; 1610 cm^{-1} (KBr). $\eta_{\text{sp}}/\text{C}$ =0.24 in 0.5 gr./dl of 98 %-sulfuric acid.

Electronic spectra

U. V spectra of polyphenyleneisoxazole and model compound were observed in 98 %-sulfuric acid. Since the polymer obtained did not dissolved in ordinary organic solvents, 98 %-sulfuric acid was used as a solvent for the U. V measurement. The reflection spectra of the polyphenyleneisoxazole was observed in powdered solid state.



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X-ray diffraction diagram

The X-ray diffraction diagrams were obtained by powder method using $\text{CuK}\alpha$ radiation at 40 kV, 20 mA, and at $2^\circ/\text{min.}$ of scanning speed, at 25, -10 , -60 , -100 , and -180°C.

Electric conductivity

Determination of electric conductivity was made on molded specimen at pressure ($50\text{kg}/\text{cm}^2$) as described previously¹⁾.

Results and Discussion

As shown in Fig. 1, the electronic spectra of polyphenyleneisoxazole in 98 % -sulfuric acid indicated the absorption at $345\text{ m}\mu$ with a shoulder at $285\text{ m}\mu$. However, model compound (from the reaction of 1 mole of terephthalohydroxamoyl chloride with 2 mole of phenylacetylene) revealed λ_{max} at $325\text{ m}\mu$ with a shoulder at $250\text{ m}\mu$.

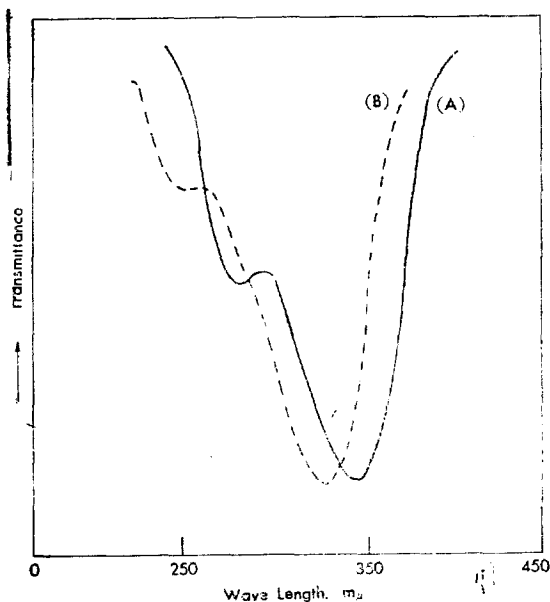


Fig. 1. The electronic absorption spectra of polyphenyleneisoxazole in 98 % -sulfuric acid (A). (B); Model compound.

Using λ_{max} value, the electron transfer energy of π electron to the lowest excitation level can be approximately determined according to the following equation²⁾.

$$\Delta E_{ph} \approx hc / \lambda_{max}$$

h ; Plancks constant
 c ; Velocity of light

ΔE_{ph} for the polymer; 3.58 e. V

ΔE_{ph} for the model compound; 4.05 e. V.

Such smaller value of red shift in the λ_{max} of the electronic spectra and smaller difference of ΔE_{ph} between the polymer and model compound indicate no evidences for long stretches of the conjugation in the polymer chain. Another spectral evidence for the shorter conjugation is from also comparatively sharp U. V absorption peak³⁾.

Fig. 2 shows the X-ray diffraction diagram of polyphenyleneisoxazole at 25°C. The sharp peak, $2\theta = 25.4^\circ$ ($d = 3.51\text{\AA}$) is comparable with those of graphite ($2\theta = 26.4^\circ$, $d = 3.38\text{\AA}$)⁶⁾, polyphenylacetylene ($2\theta = 23.7^\circ$, $d = 3.75\text{\AA}$)⁶⁾, phthalocyanine ($2\theta = 26.4^\circ$, $d = 3.38\text{\AA}$)⁷⁾, consisting of conjugated systems. If polyphenyleneisoxazole is considered to form a band structure as polyphenylacetylene and phthalocyanine, the value of 3.51\AA would be the distance between the crystalline bands. The 2θ value of 7.1° measured at 25°C did not varied with lowering temperature. However, the 2θ of others except 7.1° shifted to higher values with lowering temperature. Accordingly, the value of 7.1° may be attributable only to the polymer chain.³⁾ On the other hand, shifting of 2θ to higher value is due to the narrowing of interplanar spacing (d) of crystalline polyphenyleneisoxazole. Fig. 3 shows the narrowing of d value of 25.4° initially measured at 25°C with temperature lowering.

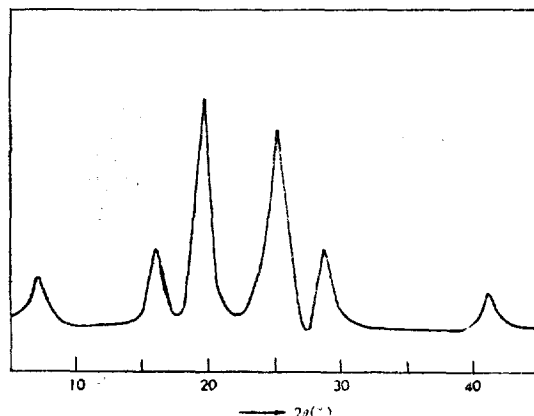


Fig. 2. The X-ray diffraction diagram of polyphenyleneisoxazole at 25°C.

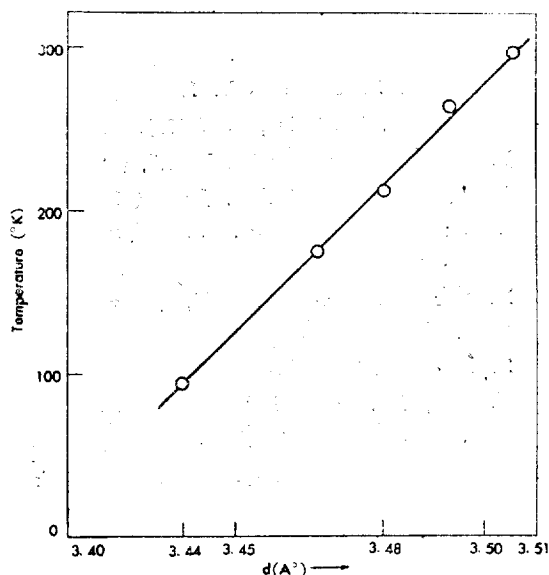


Fig 3. The narrowing of d value of 25.4° initially measured at 25°C with temperature lowering.

As shown in Fig. 3, a linear relationship was obtained between the narrowing d value of 25.4° , 2θ ; initially measured at 25°C , and temperature.

The isoxazole ring of phenylisoxazole is known to release electrons less readily than the phenyl group³⁾. This fact can be applied to polyphenyleneisoxazole, an extended form of phenylisoxazole. The phenylene group of polyphenyleneisoxazole would act as the electron donor, and isoxazole as the electron acceptor. Phenylene groups interact with isoxazole rings between the crystalline bands. Thus the charge transfer interaction would be occurred between the bands.³⁾ Substantilly, the π electrons of isoxazole ring overlap with those of phenylene group between the bands. The lower the temperature, the greater interaction would be occurred between the crystalline bands.

The occurrence of stable free radical species in polyphenyleneisoxazole³⁾ suggests the electric conductivity. Table 1. summarizes the results of the electric conductivity measured by the similar manner as described previously.¹⁾

As indicated in Table 1, polyphenyleneisoxazole shows comparatively high resistivity at a given temperature. The resistivity is increased with decreasing the electric conductivity when temperature is elevated. This shows a striking contrast with the case of polyphenyleneisoxazoline, decreasing the resistivity with temperature elevation¹⁾. Such results would be solely due to the structural feature of crystalline polyphenyleneisoxazole. As mentioned above, polyphenyleneisoxazole is consisted of smaller number of conjugation. Also the polymer would not stretch to maintain full planarity. Thus smaller overlap of π electrons between the crystalline bands would be actually resulted. The peak of λ_{max} of the electronic spectra, $345\text{ m}\mu$ in 98 % -sulfuric acid was broadened into $300\text{-}320\text{-}340\text{ m}\mu$ of reflection spectra in solid state, indicating blue shift to short wave length. This also clearly demonstrate weaker interaction between the polymer molecules in solid state. If the polymer is consisted of fully planar structure, the charge transfer interaction between the bands might be strong to increase the electric conductivity of polyphenyleneisoxazole at low temperature. However, in the present investigation, thermal motion of polymer molecule would overcome the π electron interaction between the bands at an elevated temperature. Eventually the distance, just keeping weaker interaction between the bands, would be easily aperted, then the charge transfer inteaaction

Table 1. Electric conductivity of polyphenyleneisoxazole^{a)}

Temp. ($^\circ\text{C}$)	$1/T(^{\circ}\text{K})$	$I(\text{Amp})$	$R(\Omega)$	$\rho(\Omega \cdot \text{cm})^b)$	$\sigma(\Omega^{-1} \cdot \text{cm}^{-1})^c)$
28	3.3206×10^{-3}	3.00×10^{-9}	5.267×10^9	1.151×10^{11}	8.688×10^{-12}
93	2.7311×10^{-3}	7.00×10^{-10}	2.257×10^{10}	4.932×10^{11}	2.028×10^{-12}
113	2.5897×10^{-3}	3.50×10^{-10}	4.514×10^{10}	9.863×10^{11}	1.014×10^{-12}

conductivity measured by the similar manner as described previously¹⁾.

a) Sample=89.0mg. $E(\text{charged voltage})=15.8\text{ volt}$. $l(\text{thickness of sample})=0.598\text{ mm}$. $s(\text{cross section area of sample})=1.3067\text{ cm}^2$. $s/l=21.8512$.

b) (resistivity)= $R \cdot s/l$. c) (conductivity)= $1/\rho$.

can not be possible at an elevated temperature. Rather thermal effect might be accounted as a ruling factor for the electric conductivity of polyphenyleneisoxazole under present condition.

The Author wish to acknowledge Prof. J. S. Shim for his kind encouragement. The author also indebted to Dr. Hirohashi of Chiba University, Japan, for the measurement of electric conductivity, and to Rigaku-Denki Co., for the X-ray diffraction measurement.

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