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Electrical conductivity of iodine adducts of nylon 6 and other non-conjugated polymers

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Iodine–nylon 6 adducts containing 70 to 90 wt% iodine have been prepared by heating iodine and nylon 6 at 115 and 145° C. The electrical conductivity (σ) of the adduct increases with increase in the iodine content and the iodine–nylon 6 adduct containing 90 wt% iodine and prepared at 145° C gives $\sigma = 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 25° C. Infrared, nuclear magnetic resonance (^{1}H and ^{13}C{^{1}H}), and powder X-ray diffraction analysis of the adduct show a profound change of the structure around the amide group of nylon 6 and suggest the formation of a $-\mathrm{C{=}NH^+}-$ group in the reaction of nylon 6 with iodine. The temperature dependences of σ of the idoine–nylon 6 adducts prepared at 115° C give activation energies of 51 to 92 kJ mol^{-1} depending on the iodine content. Addition of carbon powder to the iodine–nylon 6 adduct causes an increase in electrical conductivity. Other polymers (aliphatic and aromatic nylons, poly(vinyl alcohol), poly(tetrahydrofuran), poly(*N*-vinylpyrrolidone), poly(4-vinylpyridine), and poly(acrylonitrile)) which have lone pair or π-electrons also form iodine adducts containing 70 to 95 wt% iodine and the adducts show an electrical conductivity in the range of 10^{-5} to $10^{-2}\,\mathrm{S\,cm^{-1}}$. Among the iodine adducts, those of poly(vinyl alcohol) and poly(tetrahydrofuran) show electrical conductivities as high as $1.5 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ when the adducts contain about 90 wt% iodine.

1. Introduction

Since the discovery of electrical conducting iodine-doped poly(acetylene) [1, 2], the doping of π-conjugated polymers with iodine has been widely studied [3–6]. On the other hand, it is well known that various non-conjugated polymers absorb iodine to form complexes [7–22]. However, the electrical conductivity of the iodine adducts of non-conjugated polymers is reported to be low, ranging from 10^{-8} to $10^{-5}\,\mathrm{S\,cm^{-1}}$ [17–21] except for a poly(2-vinylpyridine)–iodine adduct which shows an electrical conductivity in the range of $10^{-3}\,\mathrm{S\,cm^{-1}}$ [22]. Previously we found that iodine adducts of nylon 6 showed semiconductivity when the adduct was prepared at high temperatures (such as 115 and 145° C) and the adduct contained about more than 70 wt% iodine [23]. We have expanded the work using other non-conjugated polymers to find out if iodine adducts of some non-conjugated polymers also show medium electrical conductivity ($\sigma = 10^{-4}$ to $10^{-1}\,\mathrm{S\,cm^{-1}}$) when the adducts are prepared at high temperatures and at high ratios of iodine to polymers. We now report the results.

2. Experimental details

2.1. Materials

Nylon 6, nylon 6,6, nylon 12, poly(acrylonitrile), and poly-(*N*-vinylpyrrolidone) were purchased from Polysciences Co Ltd. Poly(vinyl alcohol) was purchased from Tokyo Kasei Co Ltd. Poly(tetrahydrofuran) was prepared by a cationic polymerization of THF using $\mathrm{BF_3 \cdot Et_2O}$ as the catalyst [24]. Poly(4-vinylpyridine), poly-(isobutyl vinyl ether), and poly(vinyl acetate) were prepared by radical polymerization using benzoyl peroxide as the catalyst. Aromatic nylons were kindly donated by Professor F. Higashi of Tokyo University of Agriculture and Technology. Their inherent viscocity in concentrated $\mathrm{H_2SO_4}$ at 30° C is as follows. η_{inh}: $-(\mathrm{COC_6H_4NH})-_n$, 1.74; $-(\mathrm{COC_6H_4CONHC_6H_4NH})-_n$, 3.8; $-(\mathrm{COC_6H_4CONHC_5H_4CH_2C_6H_4NH})-_n$, 1.07; $-(\mathrm{COC_6H_4CONHC_6H_4OC_6H_4NH})-_n$, 2.31. Iodine was purified by sublimation and stored under $\mathrm{P_2O_5}$-dried $\mathrm{N_2}$. Carbon powder (Ketjen Black EC) was donated by Lion Akzo Co Ltd. Powdery nylon 6 was prepared by adding a formic acid solution of nylon 6 into vigorously stirred diethyl ether and dried under vacuum.

2.2. Preparation of iodine adducts

Powdery nylon 6 and iodine were place in a glass tube. After evacuation of the gas in the tube, it was sealed. The sealed tube was then placed in a thermostatically controlled oil bath (115 or 145° C) for 15 h. After the reaction for 15 h, some purple $\mathrm{I_2}$ vapour remained in the gas phase. However, free $\mathrm{I_2}$ was not observable after cooling the reaction system to room temperature, indicating that almost all iodine added was incorporated into the iodine–nylon 6 adduct. Iodine adducts of other polymers were prepared analogously,

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except for the iodine adduct of poly(vinyl alcohol) which was prepared by heating a mixture of a film of poly(vinyl alcohol) with iodine in an evacuated and sealed ampoule. Poly(vinyl alcohol) became insoluble in water on formation of the adduct with iodine. Iodine–polymer–carbon powder was prepared by grinding the polymer and carbon black in an agate mortar to give a powder mixture of polymer and carbon black (Ketjen Black). The mixture was then placed in a glass tube together with iodine. After evacuation of gas in the tube, it was sealed and treated in a thermostatically controlled oil bath for 15 h to obtain the composite.

2.3. Measurement of electrical conductivity and other instrumental analysis

Electrical conductivity was measured using a Takeda Riken TR-8651 electrometer. The iodine–polymer adduct (except for the iodine–poly(vinyl alcohol) adduct) was packed in a cylindrical cell (diameter = 11 mm) both ends of which were made of stainless steel (SUS 304). Through the ends of the cylindrical cell, voltage was applied and electrical measurement was performed. In the case of iodine–poly(vinyl alcohol), the electrical conductivity was measured by using a film prepared as described above; for the measurement a four-point probe method was applied. Infrared and nuclear magnetic resonance spectra were recorded on a Hitachi spectrometer 295 or a Japan Electro Optics Laboratory (JEOL) FT-IR JIR-100 spectrometer and on a JEOL Model JNM-PS-100 spectrometer or JEOL Model JNM-PET-PS-100 Fourier transform spectrometer, respectively. The X-ray diffraction patterns were recorded with a Phillips PW-1051 X-ray diffractometer. Thermogravimetric analysis was performed with a Shimadzu thermal analyser DT-30. A Cole–Cole plot was obtained using a Hokuto Denko potentiostate/galvanostate HA-301 and NF Electronic Instruments Autophase Lock-in Amplifier LI-547A, both of which were controlled by a computer.

3. Results and discussion

3.1. Iodine adducts of nylon 6

Iodine–nylon 6 adducts containing a high weight per cent (70 to 90 wt %, corresponding 2 to 8 atoms of iodine per amide unit) of iodine can be prepared by heating a mixture of I_2 and powdery nylon 6 at elevated temperatures (115 and 145° C). Although nylon 6 is known to form adducts with iodine on dipping in solutions of iodine [7–9, 21] or exposure to iodine vapour at room temperature [21], the outlook of the adduct in this study is considerably different from those prepared by the reported methods. The adducts prepared at 115° C and those prepared at 145° C and containing less than 82 wt % iodine (4 atoms of I per amide unit) are black solids, and the adducts prepared at 145° C and containing more than 87 wt % iodine (6 atoms of I per amide unit) are viscous liquid at room temperature. The latter adducts become a silver solid at -78° C, but the differential scanning calorimetry (DSC) curves of all the iodine–nylon 6 adducts reported in this study do not show any distinct exothermic or endothermic peaks in a temperature range -100 to $+150$° C.

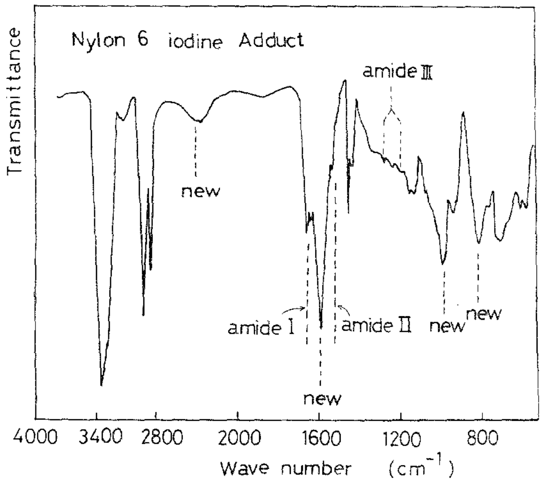
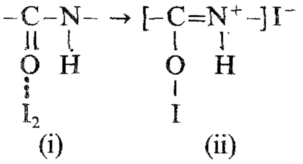


Figure 1 IR spectrum (FT–IR) of iodine–nylon 6 adduct containing 87.1 wt % iodine (6 atoms of iodine per amide unit) and prepared at 145° C. "amide I"–"amide III" show positions of amide I–amide III absorption bands of pure nylon 6.

The infrared (IR) spectrum (Fig. 1) of the adduct prepared at 145° C shows profound changes in the structure of nylon 6. The amide I (1642 cm^{-1}), amide II (1545 cm^{-1}), and amide III (1270 and 1200 cm^{-1}) absorption bands [25] of pure nylon 6 are considerably weakened or disappear, and four new absorption bands appear at 2430, 1580, 1000 and 830 cm^{-1}. The disappearance of amide I–amide III bands of nylon 6 and the appearance of a new strong absorption band (1580 cm^{-1}) in a ν(C=O) region indicate that the structure around the amide group of nylon 6 has been profoundly changed by destruction of the crystal structure (α-form) of nylon 6. The X-ray diffraction pattern of the iodine–nylon 6 adduct actually shows the disappearance of the crystalline diffraction bands of nylon 6. The new absorption band at 2430 cm^{-1} seems to be assignable to a $-C{=}NH^+-$ group [26] and its appearance suggests the formation of the following ionic structure (ii)



$$\begin{array}{ccccc} -C & -N- & \rightarrow & [-C & =N^+-]I^- \\ \| & | & & | & | \\ O & H & & O & H \\ \vdots & & & | & \\ I_2 & & & I & \\ \text{(i)} & & & \text{(ii)} & \end{array} \qquad (1)$$

Since I_2 forms adducts with various organic compounds having a lone pair, it is reasonable to assume that I_2 interacts with nylon 6 through the lone pair electrons of the amide group at room temperature [21]. Heating of the adduct may cause the chemical reaction described above. The I^- ion in (ii) may form polyiodide ion (I_n^-, $n = 3$ to 7) with I_2. Evolution of a small amount of HI during the reaction of I_2 and nylon 6 indicates that a part of $-NH-$ and/or $-CH_2-$ hydrogens of nylon 6 is substituted by iodine. The IR spectrum of the nylon 6–iodine adduct prepared at 115° C shows changes similar to that shown in Fig. 1 but, in this case, the magnitude of the change is smaller than that shown in Fig. 1.

Since the nylon 6–iodine adduct prepared at 145° C is a viscous liquid, it is amenable to nuclear magnetic

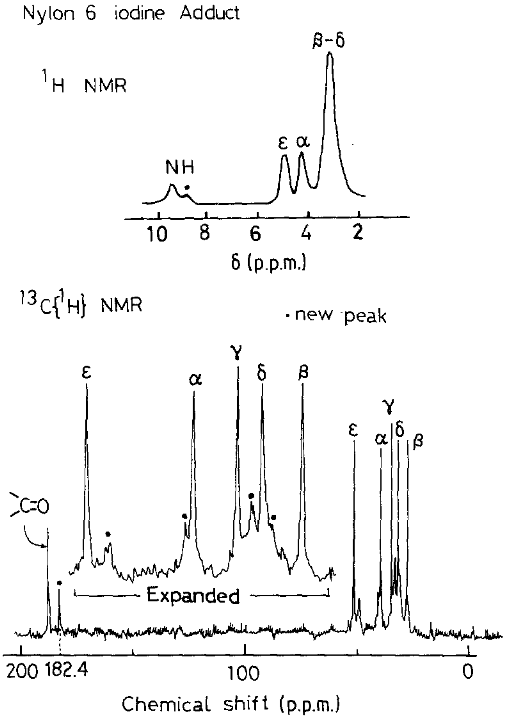


Figure 2 ^{1}H- (in $CDCl_3$) and $^{13}C\{^1H\}$ (neat) NMR spectra of iodine–nylon 6 adduct containing 87.1 wt % iodine and prepared at 145° C. α–ε CH_2 and C=O carbons are assigned from [36]. The chemical shift is referred to internal tetramethylsilane. Measured at 25° C. Peaks marked ● are new peaks.

resonance (NMR) spectroscopy as a neat sample or in solutions (as described above, nylon 6 loses crystallinity in the adduct and becomes soluble in various solvents such as $CHCl_3$ and CH_2Cl_2 which do not dissolve pure nylon 6).

As shown in Fig. 2, a $^{13}C\{^1H\}$-NMR spectrum of the iodine–nylon 6 adduct shows a new absorption peak at 182.4 p.p.m. assignable to the $-C{=}N^+-$ carbon [27] in (ii). The $^{13}C\{^1H\}$-NMR spectrum also shows several new peaks in the region of $-CH_2-$ carbons from 29 to 52 p.p.m., indicating the generation of new $-CH_2-$ units in nylon 6 according to the chemical change of the amide group. The ^{1}H-NMR spectrum (Fig. 2, upper) of the adduct shows a new absorption band at δ8.7 p.p.m. assignable to the NH^+ proton in (ii), besides a peak at δ9.2 p.p.m. of the original NH proton of nylon 6. The area ratio between the peaks at δ8.7 and δ9.2 p.p.m. equals 1 : 3.3. These IR and NMR data are compatible with formation of such a chemical species (ii).

3.2. Electrical conductivity of iodine–nylon 6 adducts

Fig. 3 shows electrical conductivity of the iodine–nylon 6 adduct. The data in Fig. 3 are obtained by a direct current method using stainless steel electrodes. A complex impedance plot (Cole–Cole plot [28] using alternating current, a.c.) of a stainless steel/iodine–nylon 6 adduct/stainless steel system (Fig. 4) demonstrates that the plot contains two arcs. The obtaining of this type of complex impedance plot containing two arcs indicates that the measuring system can be expressed by an equivalent circuit consisting of three electrical resistances and two electrical capacitances

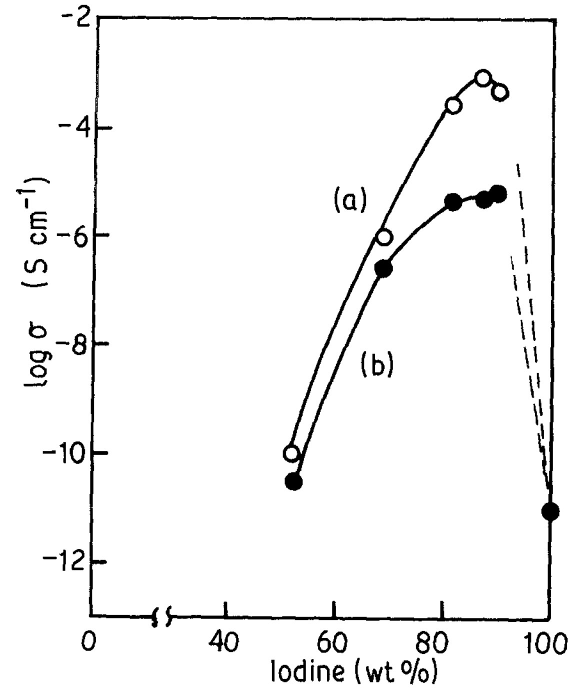


Figure 3 Electrical conductivity of iodine–nylon 6 adducts prepared at (a) 145° C and (b) 115° C. Measured at 25° C.

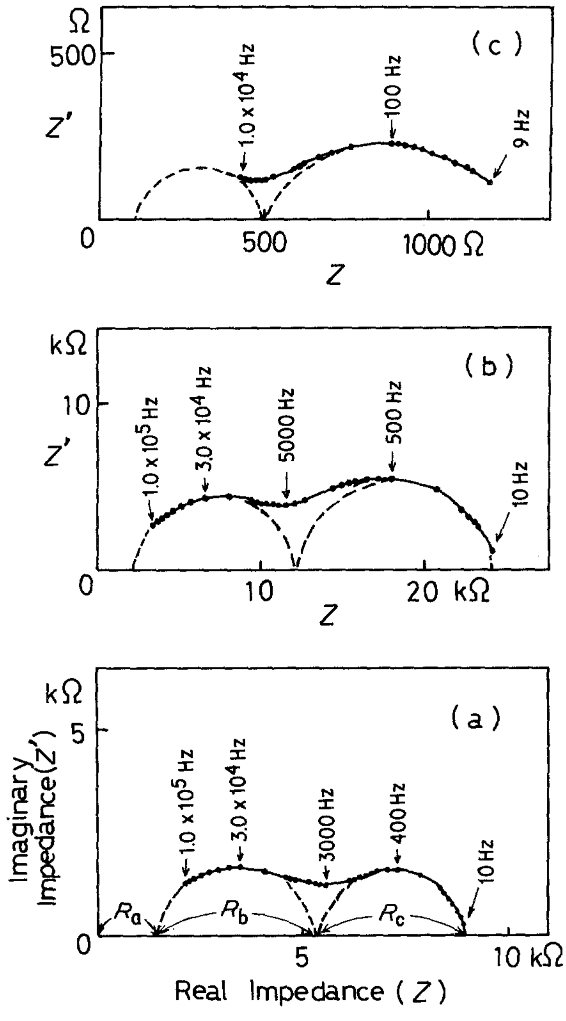


Figure 4 Cole–Cole plot of stainless steel/iodine–nylon 6 adduct/stainless steel system. Temperature for the preparation of the iodine–nylon 6 adduct and iodine content: (a) 115° C, 90.0%; (b) 115° C, 81.8%; (c) 145° C, 81.8%. Pellets of iodine–nylon 6 adducts were used; diameter ~ 11 mm, thickness ~ 2 mm. The frequency in the figure shows frequency of applied alternating current.

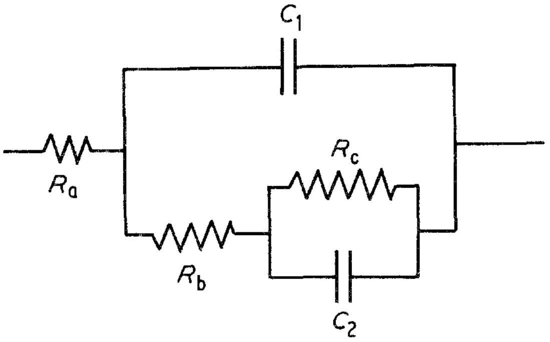


Figure 5 Postulated equivalent circuit.

(e.g. an equivalent circuit shown in Fig. 5) [29]; the R_a, R_b, and R_c in Fig. 4 correspond to the three electrical resistances, respectively. In the direct current (d.c.) method, the electrical resistance of the measuring system is obtained as a sum of R_a, R_b, and R_c, and the data shown in Fig. 3 are based on the summed value, $R = R_a + R_b + R_c$. Watanabe and co-workers [30–32] proposed an equivalent circuit analogous to that shown in Fig. 5 to analyse electrical conductivity of a polymer-based material. If the present measuring system can be expressed by the equivalent circuit shown in Fig. 5, the R_b part is likely to reflect the real electrical resistance of the iodine–nylon 6 adduct as suggested by Watanabe and co-workers concerning the electrical conductivity of their material, whereas R_c is likely to reflect an interfacial electrical resistance originating from the interface formed between stainless steel and the iodine–nylon 6 adduct. If we assign the R_b part to the real electrical resistance of the iodine–nylon 6 adduct, the real electrical conductivity of the adduct becomes two to three times larger than the value shown in Fig. 3.

As shown in Fig. 3, the apparent electrical conductivity (or d.c. electrical conductivity) of the iodine–nylon 6 adduct steeply increases with increase in the iodine content, although iodine itself is an insulating material. In the case of iodine–nylon 6 adduct prepared at 145° C, the electrical conductivity reaches as high as $10^{-3}\,\mathrm{S\,cm^{-1}}$, which is a considerably large value for non-conjugated polymer-based materials and higher than or comparable to electrical conductivity of iodine adducts of some π-conjugated polymers such as poly(*p*-phenylene) ($\sigma \sim 10^{-5}\,\mathrm{S\,cm^{-1}}$) [19] and poly(2,5-thienylene) ($\sigma = 10^{-1}$ to $10^{-2}\,\mathrm{S\,cm^{S-1}}$) [3–6].

The electrical conductivity (σ) obeys the following Arrhenius type equation

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (2)$$

and the values of σ_0 and E_a for the iodine–nylon 6 adducts prepared at 115° C are summarized in Table I. The activation energy for the electrical conduction is considerably larger than the activation energy obtained for iodine-doped π-conjugated poly(2,5-thienylene) [3–6] and poly(acetylene) [1, 2], indicating the presence of a higher energy barrier for the electrical conduction in the present system.

TABLE I Parameters (σ_0 and E_a) for the electrical conductivity of iodine-nylon 6 adduct prepared at 115° C*

Iodine (wt %)	N[†]	σ_0 ($\mathrm{S\,cm^{-1}}$)	E_a ($\mathrm{kJ\,mol^{-1}}$)
69.2	2	1.3×10^3	92
81.8	4	2.0×10^4	67
87.1	6	1.9×10^6	57
90.0	8	7.1×10^9	51

*Based on temperature dependence of the electrical conductivity measured at 10–35° C.

[†] Number of iodine atoms per amide group.

Although we do not have enough evidence to assign the present electrical conduction to electron conduction or ionic conduction, we prefer the electron conduction on the basis of the following observations.

1. The electrical conductivity shows only a minor time dependence. Moreover, *i–V* correlation (voltage range: −1 to +1 V) for the present iodine–nylon 6 adduct shows a linear line and no hysteresis of the *i–V* correlation. Ionic conduction usually shows time-dependent electrical conductivity and hysteresis of the *i–V* correlation.

2. If we assume the equivalent circuit shown in Fig. 5 and assign the R_c part in Fig. 4 to the interfacial resistance originating from the interface formed between the stainless steel electrode and the iodine–nylon 6 adduct, the value of R_c for the iodine–nylon 6 adduct prepared at 145° C ($R_c = \sim 10^3\,\Omega$, Fig. 4c) is considerably smaller than the interfacial observed for the Pt/LiX–poly(alkylene oxide) adduct/Pt system [30–32]. In the latter system, the electrical conduction of the LiX–poly(alkylene oxide) is attributed to ionic conduction and platinum serves as a blocking electrode which neither generates nor receives ionic carriers; in this system the interfacial resistance is much larger than the electrical resistance of the Li–poly(alkylene oxide) adduct and its typical value is about $10^5\,\Omega$. If the electrical conduction of the present iodine–nylon 6 adduct is attributed to ionic conduction, the stainless steel electrode is also considered to serve as the blocking electrode.

Since I^- exists in the iodine–nylon 6 adduct and an I_n interconnection network seems to be formed in the adducts with high concentrations of iodine, the movement of an electron through the iodine site is suggested. The moving of electrons or holes assisted by the cation centre formed by Reaction 1 (e.g. jumping of the positive charge centre of (ii) between polymers) is also conceivable.

3.3. Electrical conductivity of iodine–nylon 6–carbon composite

Fig. 6 shows the electrical conductivity of the iodine–nylon 6–carbon powder composite prepared at 115° C. As shown in Fig. 6, when the wt % carbon powder per nylon 6 is below 5%, the electrical conductivity of the composite is very low at low contents of iodine and increases with increase in iodine content. On the other hand, when the carbon content is higher then 10%, nylon 6–carbon powder composite itself shows electrical conducting properties even without iodine, presumably due to the formation of a carbon network in the nylon 6–carbon mixture [33]. In cases

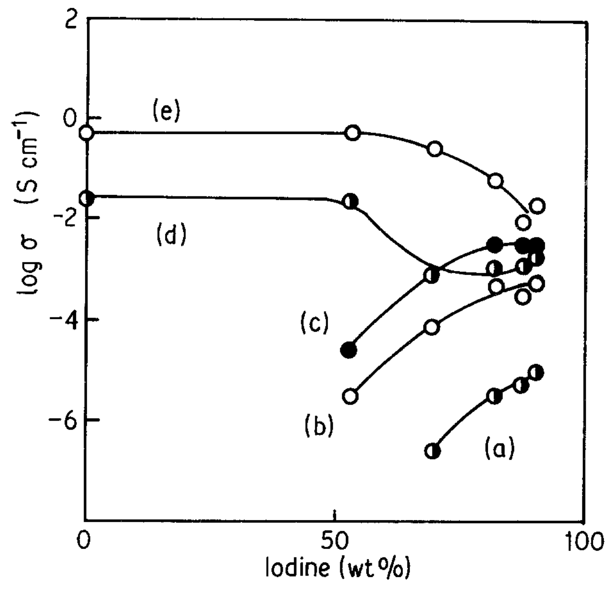


Figure 6 Electrical conductivity of iodine–nylon 6–carbon powder composite prepared at 115° C. Wt % carbon powder per nylon 6: (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%. Abscissa shows wt % iodine in the iodine–nylon 6 adduct in the composite. Measured at 25° C.

where the composites contain more than 10 wt % carbon powder, addition of iodine causes a decrease of electrical conductivity by breaking the carbon network. At high weight per cents (80 to 90 wt %) iodine, the iodine–nylon 6–carbon powder composite containing more than 10 wt % carbon per nylon 6 shows similar electrical conductivity to that of iodine–nylon 6 adduct without carbon. A similar trend is also observed with iodine–nylon 6–carbon powder composite prepared at 145° C (Fig. 7).

3.4. Electrical conductivity of iodine adducts of non-conjugated polymers other than nylon 6

Other nylons, including aliphatic (nylon 6,6 and nylon 12) and aromatic $(\text{-COC}_6\text{H}_4\text{NH})\text{-}_n$, $\text{-(COC}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{NH}))_n$, $\text{-(COC}_6\text{H}_4\text{CONHC}_6\text{H}_6\text{CH}_2\text{C}_6\text{H}_4\text{NH)-}_n$, and $\text{-(COC}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH)-}_n$; C_6H_4 = *p*-phenylene) nylons, also form adducts containing more than 80 wt % iodine when they are heated at elevated temperature (115 to 145° C), and the adducts formed show electrical conductivity of about 10^{-5} to $10^{-3}\,\text{S cm}^{-1}$.

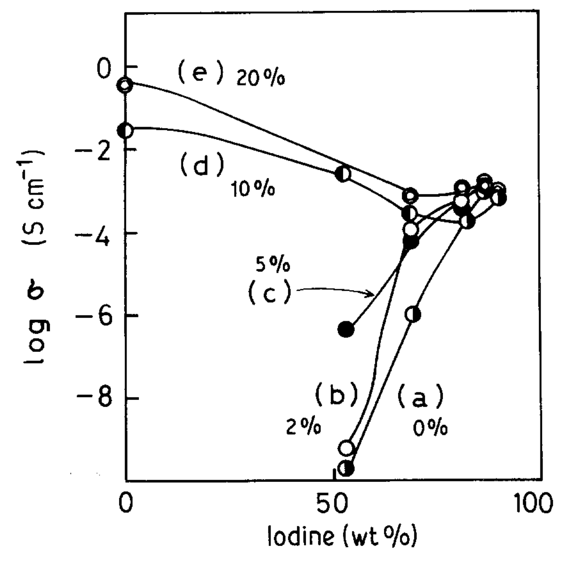


Figure 7 Electrical conductivity of iodine–nylon 6–carbon powder composite prepared at 145° C. Wt % carbon powder per nylon 6: (a) 0%, (b) 2%, (c) 5%, (d) 10%, and (e) 20%.

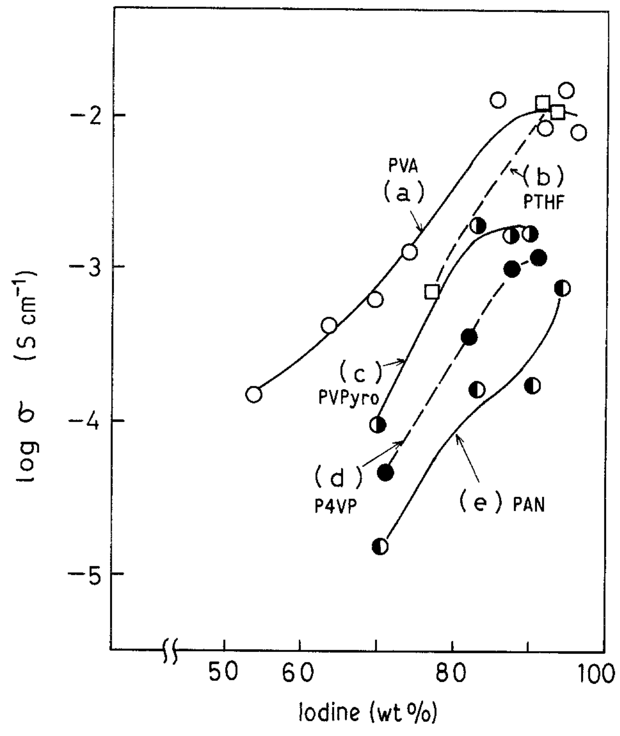


Figure 8 Electrical conductivity of iodine–polymer adducts prepared at 115° C. Polymer: (a) poly(vinyl alcohol); (b) poly(tetrahydrofuran); (c) poly(*N*-vinylpyrrolidone); (d) poly(4-vinylpyridine); (e) poly(acrylonitrile). Measured at 25° C.

Polymers other than nylons also form similar adducts with iodine at elevated temperatures when they have lone pairs or π-electrons. Fig. 8 shows the electrical conductivity of the iodine adducts of several polymers. As seen in Fig. 8, poly(vinyl alcohol), poly(tetrahydrofuran) (or poly(oxybutylene)), poly(*N*-vinylpyrrolidone), poly(4-vinylpyridine), and poly(acrylonitrile) form iodine adducts containing more than 90 wt % iodine, and the adducts show an electrical conductivity of about 10^{-3} to $10^{-2}\,\text{S cm}^{-1}$. The electrical conductivity of the iodine adducts of poly(vinyl alcohol) and poly(tetrahydrofuran) containing about 90 wt % iodine ($\sigma = \sim 1.5 \times 10^{-2}\,\text{S cm}^{-1}$) is the highest electrical conductivity reported for iodine adducts of non-conjugated polymers. The iodine adduct of poly(2-vinylpyridine) reportedly shows [22] electrical conductivity similar to that of the iodine adduct of poly(4-vinylpyridine) shown in Fig. 8. It is noteworthy that iodine adducts of poly(vinyl alcohol), poly(tetrahydrofuran), and poly(*N*-vinylpyrrolidone) have higher electrical conductivity than that of iodine adducts of poly(vinylpyridine)s which are used as cathodes of lithium–iodine solid electrolyte galvanic cells due to their electric conducting properties [22]. The *i–V* correlation of iodine–poly(vinyl alcohol) adducts shows a linear slope and no hysteresis.

Iodine adducts of poly(isobutyl vinyl ether) (wt % iodine = 88.4) and poly(vinyl acetate) (wt % iodine =

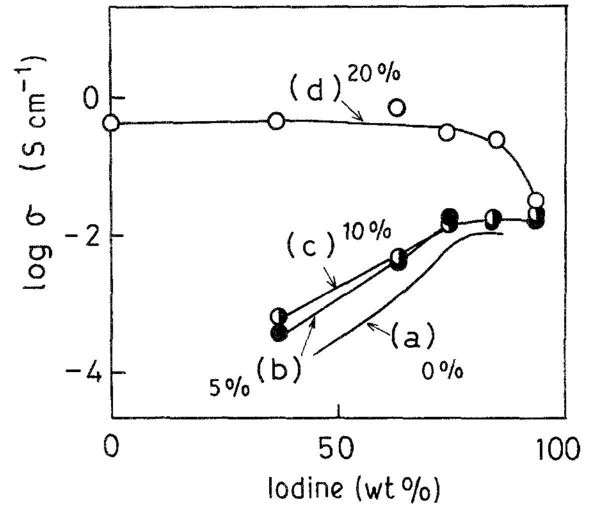


Figure 9 Electrical conductivity of iodine–poly(vinyl alcohol)–carbon powder composite prepared at 115° C. Wt % carbon powder per poly(vinyl alcohol): (a) 0%, (b) 5%, (c) 10%, and (d) 20%. Measured at 25° C. Abscissa shows wt % iodine in the iodine–poly(vinyl alcohol) adduct in the composite.

89.9) also show semiconductivities of 2.3×10^{-2} and 2.3×10^{-4} S cm^{-1}, respectively, at 25° C.

Fig. 9 shows the electrical conductivity of an iodine–poly(vinyl alcohol)–carbon composite prepared at 115° C. Similarly to the case of iodine–nylon 6–carbon composite, the electrical conductivity increases with increase in carbon content, and the dependence of the electrical conductivity on wt % iodine in the iodine–poly(vinyl alcohol) adduct is similar to that observed for the iodine–nylon 6–carbon composite shown in Fig. 6.

Most of the iodine–polymer adducts and iodine–polymer–carbon composites described above are stable on standing at room temperature. For example, after standing iodine–nylon 6 adducts in sealed glass tubes at room temperature for 1 yr, no apparent degradation of the adducts was observed and only minor amounts of I_2 were released from the adducts. However, the iodine–poly(vinyl alcohol) adduct was somewhat unstable when it contained more than 75 wt % iodine, and release of I_2 from the adduct was observed after 1 yr.

Polymers having neither lone pairs nor π-electrons (e.g. poly(ethylene) and poly(propylene)) also absorb iodine to some extent; however, amounts of iodine absorbed by the polymers are small even after reaction at elevated temperatures (115 and 145° C) and the iodine adducts show only low electrical conductivities below 10^{-10} S cm^{-1}.

4. Conclusion and remarks

Nylon 6 and other non-conjugated polymers which have lone pairs or π-electrons form iodine adducts containing more than 70 wt % iodine at elevated temperatures. The adducts show electrical conductivity in the range 10^{-5} to 1.5×10^{-2} S cm^{-1} at 25° C. The value of the electrical conductivity is considerably higher than reported values for previously reported iodine adducts of polymers which were prepared mostly at room temperature and contained lesser amounts of iodine. On addition of carbon powder, the iodine–polymer adducts show higher electrical conductivity. Owing to the electrical conducting properties of the present iodine–polymer adducts, some are usable as positive electrodes of Li|LiI|iodine solid electrolyte galvanic cells. Among the adducts tested, the iodine–nylon 6 adduct is most suitable for the galvanic cell discharged at 500 kΩ load [34, 35] and the iodine adduct of poly(tetrahydrofurance) to the galvanic cell discharged at 10 kΩ load.

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