Review

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Molecular iodine/polymer complexes

Abstract: A unique feature of molecular iodine by far, is its ability to bind to polymeric materials. A plethora of natural and synthetic polymers develop complexes when treated with molecular iodine, or with a mixture of molecular iodine and potassium iodide. Many unexpected findings have been encountered upon complexation of iodine and the polymer skeleton, including the color formation, the polymer morphology changes, the complexation sites or regions, the biological activity, and the electrical conductivity enhancement of the complexes, with polyiodides (I$_n^-$), mainly I$_3^-$ and I$_5^-$, as the actual binding species. Natural polymers that afford such complexes with iodine species are starch (amylose and amylpectin), chitosan, glycogen, silk, wool, albumin, cellulose, xylan, and natural rubber; iodine-starch being the oldest iodine-natural polymer complex. By contrast, numerous synthetic polymers are prone to make complexes, including poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), nylons, poly(Schiff base)s, polyaniline, unsaturated polyhydrocarbons (carbon nanotubes, fullerenes C$_{60}$/C$_{70}$, polyacetylene; iodine-PVA being the oldest iodine-synthetic polymer complex.

Keywords: antibacterial activity; complexation; conductivity; doping; molecular iodine; polymers.

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1 Introduction

Halogenation is an integral part of organic reactions. Halogenated organics are useful materials for a wide range of applications, including solvents in organic synthesis, fire retardant substances, microorganism killing compounds (e.g., bactericides, pesticides, insecticides), polymers with non-stick coating properties such as polytetrafluoroethylene (PTFE, Teflon) and many others. Whereas PTFE is reputed for its safe uses, polychlorinated and polyiodinated molecular compounds are particularly highly toxic, and some of them are even suspected cancer agents. Halogenated compounds, mainly polyhalogenated ones R-(X)$_n$ (X=F, Cl, Br, I) are prominent chain transfer agents in radical polymerization, employed mainly as telogens in telomerization or oligomerization [1, 2]. Particularly, iodocompounds are highly attractive as potential intermediates for the synthesis of macromolecular molecules, because of the good leaving property of iodine atom [3], as in controlled radical polymerizations (CRP): [nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT)] [2]. Also, alkyl iodides are efficient alkylating agents in the homolytic alkylation of heteroatom bases, such as pyridine derivatives [4].

Noteworthy, is the upsurge in interest in the chemistry of polyvalent organic iodine reagents, starting early in the 1990s, and since then, a myriad of reports on the use of such compounds in organic synthesis have been published [5].

Halogenation is traditionally carried on in Lewis acid-Lewis base reactions, where the halogen (X$_2$=Cl$_2$, Br$_2$, I$_2$) acts as the electrophilic species (Lewis acid) and the electron-rich organic compound as the nucleophilic species (Lewis base), or via a nucleophilic or homolytic substitution with a halide ion or radical (X, X$^-$). Of the halogens, iodine has been also valorized as an effective Lewis acid catalyst in many reactions. Indeed, literature is surfeited with organic reactions that involve the use of molecular iodine, as it is an inexpensive, easily available, and environmentally benign catalyst [6–8].

Uses of iodine are extended to pharmaceutical and medical applications, sanitation or disinfection [9], animal feed [10], catalysts [7], inks, dyes, photographic equipment, doping agent for polymers as discussed below, and stabilizers [11]. The other importance of molecular iodine is its germicidal activity against a wide range of bacteria and viruses [12]. Moreover, its medicinal activity has been highly claimed [13]. It is worth recalling that more than 95% of total iodine necessary for humans is accumulated in the thyroid gland. Iodine is slightly soluble in water.
and its hydrosolubility can be enhanced in the presence of iodide ions, where the formation of polyiodides such as $\mathrm{I}_n^-$ ($n=3, 5, 7, 9, \ldots$) occurs. Its solutions are brown in polar solvents (water, ketones, alcohols, carboxylic acids) and violet in apolar solvents such as $\mathrm{CCl}_4$, benzene, and aliphatic hydrocarbons [11].

Iodine is one of the components of Wijs reagent used for the estimation of the iodine value (IV) of fats and oils [14, 15]; Wijs reagent is a solution of iodine monochloride in acetic acid and can be prepared from a mixture of iodine trichloride and iodine.

Halogenation of polymers with halogens was confined chiefly to chlorination and bromination, affording chlorinated/brominated polymers, such as chlorinated poly(vinyl chloride) (CPVC), chlorinated polyethylene, chlorinated polystyrene, chlorinated polychloroprene, chlorinated rubber, and brominated natural rubber (BNR). Recently, a fascinating finding was the reaction of submicron-sized polymer particles (PSE) containing imidazoline selenones, with halogens, to form adducts with vivid color-change from white to red-orange (red-orange with I$_2$, yellow with Br$_2$, and yellow with faint red color with Cl$_2$) [16].

As an ordinary step in organic synthesis research and in chemistry laboratory, iodine vapor is routinely employed in thin layer chromatography (TLC) to visualize the different components of a mixture being analyzed [17]; this feature is based on the ability of these components to sorb iodine molecules, giving rise to colored spots. A reaction of iodine with sodium azide named “iodine-azide reaction” is another means to detect amino acids in the reaction of iodine with sodium azide named “iodine-azide reaction” is another means to detect amino acids in the

2 Molecular iodine in polymer complexation

Acting as a Lewis acid, molecular iodine reacts readily with electron-rich molecules via a charge transfer mechanism, to form charge transfer complexes (CTCs) [20], as confirmed by electron spin resonance spectroscopy [21]. Electron-rich molecules, acting as Lewis bases, include those bearing atoms with lone pairs and aromatic ones. A deep blue-black precipitate is formed when iodine is mixed with some aromatic hydrocarbons, such as azulene, guaiazulene, and acepleiadylene [21]. A good example of a molecule having lone pairs is 5-methyl-1,3,4-thiadiazoline-2-thione ($\mathrm{C}_4\mathrm{H}_4\mathrm{N}_2\mathrm{S}_2\mathrm{I}_2$), a potential antithyroid drug, that can form an $n\sigma^*$ complex with iodine [22]. Such $n\sigma^*$ complex forming was evaluated in the spectro-photometric determination of nitrogen-containing drugs with antifungal, antidepressant, antihistamine, and $\beta$-adrenergic properties, such as omeprazole, lansoprazole, rabeprazole, famotidine, terbinafine, escitalopram oxalate, esmolol and oxprenolol [23]. The iodine-induced color property was applied to the detection of bacterial penicillinase [24]. Sen and his co-workers [25] evaluated the complexes between molecular iodine and a number of conjugated polyenes such as $\beta$-carotene, lutein, retinonic acid and $\beta$-apo-8′-carotenal, as cathodes in solid-state batteries.

This complex-forming phenomenon has been exploited in different ways. For example, the iodine was used to fractionate the coal tar pitch [26], to modify its rheology and carbonization behaviors [27–30], and to enhance the electrical property of asphaltene's [31]. Also, the iodine complexing propensity towards cyclodextrin in a host-guest chemistry led to the application of the latter molecule in nuclear waste management [32]. In the same way of the host-guest mechanism, it was found that gossypol, a phenolic yellow pigment extracted from cotton seeds with a zeolite-like structure, was able to form a brown crystal complex with molecular iodine as (gossypol)$_n$I$_2$ [33]. Indeed, the host-guest interaction was quantified with the zeolite-molecular iodine system, formed with sublimed iodine [34]; the iodine was found to diffuse in $\alpha$ and $\beta$ voids of the zeolite framework, accompanied with a color change of samples from white (zeolite A) to dark or brown-red.

As discussed below, the deep blue color of the complex was common for the iodine-starch complex for over 100 years, routinely explored as an indicator in iodometry (e.g., in the kinetics measurement of organic reactions, and in the determination of chlorine concentration in water). Recently, complexation of iodine by amyllose was claimed to be efficient in combating the iodine deficiency disorders [35].

Earlier, Bartlett and Schmidt [36] reported the germicidal property of poly(ethylene oxide)-based nonionic surfactant-iodine complex.

As far as medical advancement is concerned, the iodine-albumin complex was very effective in disinfecting blood, blood components, plasma, serum, cell concentrates, and clotting proteins [37]. It is worth noting the iodine staining role in resolving the arrangement of muscle fibers, as recently reported [38]. Most importantly
is the complexation of molecular iodine with organic polymers, both natural and synthetic, affording adducts with valuable uses and applications. Polymers having electron-rich sites within their matrices or their pendant moieties are prone to bind iodine. Yet, natural polymers were limited to starch and its components (amylose and amylpectin), chitosan (and not chitin, the polymer source), glycogen and silk. However, synthetic polymers were numerous, with a particular emphasis on poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP) and polyamides (nylons). The intrinsic properties of some polymers were remarkably enhanced upon iodine treatment. Indeed, the antimicrobial activity [39] and conductive properties [40] of polymers were the most investigated properties after iodination.

Practically, the realization of an iodine-polymer complex can be done either by immersing the polymer in an aqueous solution of I₂/KI, by exhibiting it to molecular iodine vapor, or by conducting the polymerization in the presence of iodine (an in situ doping). Because iodine is sparingly soluble in water, aqueous KI solution is routinely added to the molecular iodine/polymer system, to ensure iodine solubility, generating polyiodides Iₙ⁻, which are the real complexing species; the aqueous solution of molecular iodine/KI is well-known as “Lugol’s iodine” or “Lugol’s solution” and “iodine tincture”. It is worth recalling that, in the early 1900s, this solution was widely used to supplement the thyroid gland in order to function properly [41].

For a matter of reading clarity, the iodine-polymer system, herein designated I₂-polymer, is often interchangeably used under the following terms, regardless of the way by which the iodine is bound to the polymer: iodine-polymer complex, iodine-bound polymer, polymer-supported iodine, iodine-polymer adduct, iodine-sorbed polymer, iodine-loaded polymer, iodine-treated polymer, iodine-doped polymer, and I₂-polymer.

### 2.1 Iodine-natural polymer complexes

#### 2.1.1 Iodine-starch complexes

The first iodine-organic polymer complex is undoubtedly iodine-starch, which was discovered in 1814 by two French chemists, Jean-Jacques Colin and Henri-François Gaultier de Claubry [42], and confirmed one year later by Friedrich Stromeyer, a German chemist. The feature of this complex at that time was its dark-blue color that was observed in 1886 by the Swiss chemist, Hans Heinrich Landolt [43], in reactions called “iodine clock reaction” or “Landolt reaction”. Earlier, François-Vincent Raspail, the French scientist, valorized this color to test for starch in plants, as indicated in his reports of 1825 [44]. From the date of its discovery up until now, there have been an uncountable number of reports tackling various aspects of this complex, hinting at its complexity.

Structurally, starch consists of the linear and helical (coil)amylose (10–20%; molecular weight=10⁴–10⁶) and the branched amylpectin (80–90%; molecular weight=10⁴–10⁹) (Figure 1). Yet, the dark blue color of iodine-starch is mainly due to the iodine-amylose complex absorbing at λₘₐₓ around 650 nm, because the iodine affinity towards amylose is about 20% and <1% towards amylpectin. The iodine-amylpectin adduct appears reddish-purple, absorbing at λₘₐₓ of about 540 nm. It has been shown in many reports that the polyiodides Iₙ⁻ (n=3, 5, 9…) in the iodine-amylose complex are occluded in the helical cavity of the amylpectin and arranged in a linear array, parallel to the helical axis [45–49]. Ono [50] proved that λₘₐₓ of the amyllose-iodine complex shifted toward shorter wavelengths and the resonating chain length became shorter with increasing iodide concentrations, results arising from the breakdown of the polyiodine chains by the penetrated iodide ions.

However, the dark blue color is caused mainly by the polyiodide Iₙ⁻ in the iodine-amylose complex and the reddish-purple color by I₃⁻ in amylpectin. Yet, in 1948, Gilbert and Marriott [51] advanced potentiometric evidence of the involvement, at a very low percentage adsorption and low iodide concentration, of three iodine molecules and two iodine ions (3I₂·2I⁻) in the amyllose complex. Also, at higher iodide concentrations, the ratio of iodide ions to iodine molecules increased until it was at least equal to one, to be (I₃⁻)ₙ; this change was accompanied by the appearance of a slightly purple tinge in the blue of the complex. It was further suggested that the red-staining starches would contain less than eight atoms of iodine and iodide per molecule. Reddy et al. [52] studied the HI₃·2C₆H₅CONH₂ complex and concluded that this could be taken as a model for the iodine-starch complex; it was therefore suggested that a single chain of Iₙ⁻ ions is the chromophore in the blue iodine-starch complex. Other models of closer structures to amylose, such as cyclohexa-amyllose (α) (Schardinger α-dextrin, or α-cyclodextrin), maltodextrin, maltotetraose, maltopentadecaose were studied [53–57]; from these studies, it was found that α-I₂ was formed in the absence of an iodide ion and α-I₃⁻ in its presence.

The color difference observed between iodine-amylose and iodine-amylpectin complexes was also assigned to the difference in the structures [58], the branch chain...
length [59], and the branching points in amylopectin that may induce steric hindrance [60]. Indeed, for a degree of polymerization (DP) in amylopectin of 15 (15 glucose units), no complexation occurred at any temperature, but for a DP higher than 30, considerable iodine can be bound to amylopectin either at 1.5°C or 20°C [59]. By potentiometric and spectrophotometric means, Mould and Synge [61], and Mould [62] observed the earlier complexation of iodine/iodide with enzymatic hydrolys products of amylose, the hydrolysates being the dextrins with different molecular weights, and the complexes were of different colors; an electrophoretic fractionation was employed to separate the dextrins. In fact, iodine complexes with dextrins of DP<10 were scarcely staining, those of DP=10–25 were orange, those of DP=25–40 were red, and those of DP=40–130 were blue.

The effect of iodine on the intrinsic viscosity \([\eta]\) of the starch was investigated by Liang and his co-workers [63]. The results were that \([\eta]_{\text{amylose}}\) rose with iodine concentration, suggesting a stiffening of the helix without a basic change in the conformation, and that the amylose molecule was extended by absorption of iodine in quantities up to a ratio of one molecule per turn of the helix. Such rigidity was endorsed by the reduction of the temperature dependence of \([\eta]_{\text{amylose}}\) on complexing. The authors strongly believed that the most possible explanation of the iodine-starch interaction was through the dipolar forces, and not between iodine and the oxygen atom of amylose; the dipolar forces would rigidify the helical structure of the molecule and increase \([\eta]\).

Knutson [64] demonstrated the possibility of distinguishing between several botanic sources of starch by means of UV-visible measurements of their iodine-amylose complexes; for example, the absorptions of the complexes from maize, potato, corn, and tapioca were measured as 616, 622, 615, and 612 nm, respectively. Electrochemical studies showed that, while iodine is electrochemically active, the iodine-starch in the absence of an iodide ion was inactive [65]. In the TLC technique, flushing iodine vapor-treated plates with an aqueous solution of starch (1–2%) is commonly performed for a better visualization (the blue color formation) and detection of components [17]. Manion et al. [66] reported a method for quantifying iodine in the iodine-starch complex, up to a limit of 5 wt% of iodine. It consisted of reducing all iodine species into iodide ions which could be derivatized to ethyl iodide using \(\text{Et}_3\text{O-BF}_4\) in CHCl₃, and the amount of ethyl iodide was assessed by gas chromatography analysis. Starches from different botanical origins were tested in this experiment. In general, the linear polysaccharides tend to give a blue color when iodinated, and this color disappeared by diluting with water or by heating the mixture up to 100°C; the blue color may be restored upon cooling to room temperature or lower. The blue-colored iodine-starch complex was employed as a colorimetric means for the determination of amylase [67, 68] and its degradative property [69].
in the determination of β-lactamase activity [70], and in the detection of water vapor [71].

Four fundamental Raman lines were observed at 159, 111, 55 and 27 cm⁻¹ corresponding to the I⁻ in amyloses with DP from 20 to 100 [72]. Kim [73] attributed these bands to the symmetric modes of either the (I⁻·I⁻)ₙ or (I⁻)ₙ linear chain; the former consists of a weakly coupled linear chain of (I⁻)ₙ structure, while the latter, (I⁻)ₙ, is a tightly bound chain. Handa and Yajima [74] found that the color variation of the triiodide species in amylose was dependent on the degree of polymerization of amylose. In the circular dichroism spectrum (CD), the shoulder around 480 nm developed for a DP range of 10–30. Second, the blue color developed critically from DP=30 and deepened on going to DP=100. Third, the deep bluing was observed for DP>100.

The species bound to amylose depended on the iodide concentration; based on magnetic circular dichroism (MCD) and the liquid-liquid distribution technique, they were found to vary from I⁻ at 10 mm KI to I₁⁻ at 0 m KI [75], and 2.7 to 3.0 of D-glucosyl residues were required for including one iodine atom. Moreover, the authors stated that the species responsible for the blue color were I⁻ (I⁻·I⁻), I⁻·I⁻ and I⁻·I⁻·I⁻. Earlier, however, and based on potentiometric/spectrophotometric titration methods, Knutson et al. [76] showed that the bound species varied from I⁻ at 100 mm KI to I₁⁻ at 0.5 mm KI. In the latter report, the amount of iodine bound to 100 mg amylose was 30 mg, and the mass ratio of iodine to amylose in the complex was one I⁻ per five glucose residues based on the potentiometric excess-iodine (EI) titration method.

Saenger [77] meticulously worked out the structure of the iodine-starch complex and put forward clear-cut answers as to the iodine species involved in the iodine-amylose complex. Analyses by Raman and Mössbauer spectroscopy clearly demonstrated that the prevailing iodine form was I⁻. Later, Fonslick and Khan [78] and Minick et al. [79] surprisingly ruled out the existence of the negatively iodine species I⁻ for neutral iodine units (I⁻). This evidence was the magnitude of the reaction (−110 kJ) for every mole of I⁻ in the amylose helix), compared to the binding energy of I⁻ (−149 kJ/mol), which indicated that the dissociation of I⁻ could not occur. It was deduced from quantum mechanical calculations that polyiodine units I⁻, with an interiodine distance of 3.0 Å, were responsible for the characteristic UV-visible absorbance bands of the iodine-starch complex. Also, the polymeric unit responsible for the characteristic blue color of the complex was proposed to be (C₆H₁₀O₅)ₚ·I⁻.

Saibene and Seetharaman [80, 81] and Saibene et al. [82] demonstrated the effect of moisture on the complexation of iodine with starch in its granule form and of different amylose contents. The results indicated the ability of granular common corn starches (CCS) to bind iodine at moisture contents as low as 8%, and the iodine binding in a native granule requires a critical mobility level of the linear molecules. The water molecules plasticize the starch, thus increasing the ability to bind iodine by the formation of single helices. A moisture content of about 13% promoted a disruption of the crystallinity within the granules. According to X-ray analysis, at moisture contents in the range of 12–20%, CCS bound iodine more effectively than potato starch, which may be related to the greater amount of water associated with the crystalline regions of the latter starch. In addition, iodination reduced the crystallinity of potato starch granules (PS) more strongly than it did in CCS ones, a result that is consistent with a greater amylose content in the crystalline structures of the two starches. Besides, the extents of lintnerization of CCS and PS proved the involvement of amylose in the B-type crystallites of PS, and not in the A-type crystallites of CCS.

Yu and his collaborators [83] proved the occurrence of different iodine forms when the complexation occurs between I⁻/KI and potato amylose by Raman and UV-visible spectroscopy. Besides the primary forms I⁻ and I₁⁻, polyiodide ions such as I₃⁻, I₄⁻, I₅⁻, and I₁₃⁻ were also detected and absorbed at 460–480, 560–590, 660–700, and 710–740 nm, respectively. The extents of these species depended on the I⁻/KI concentration ratios; higher iodide concentrations favored shorter polyiodide chains.

Miyajima et al. [84] investigated the influence of iodine treatment on the carbonization of starch. To this end, starch film was treated with iodine at 100–150°C for 24 h, followed by carbonization at 700–1000°C under nitrogen stream. The char yield at 800°C was in the range of 30–35% for an iodine content of 110–115 wt%, and for iodine treatment temperature of 120–140°C. The char doubled in yield by iodine treatment. The carbonization of the iodine-treated starch resulted in the formation of a dense and microporous carbon film with an uneven surface. From the adsorption isotherms, the micropore area (A) and micropore volume (V) for the iodine-treated starch were larger than those for the non-treated starch at all carbonization temperatures. Particularly, they were about twice those for the carbonization at 700°C, that is, 650 m²/g and 0.22 ml/g vs. 305 m²/g and 0.09 ml/g. Iodine treatment entailed thermal stability to starch; while starch started to lose weight around 350°C, the iodinated one lost weight gradually up to 650°C. In addition, the different fragments from the carbonization
of starch were detected at temperatures <350°C when treated with iodine.

2.1.2 Iodine-cellulose derivatives complexes

Although it has been claimed that cellulose (Figure 2A) does not form a complex with iodine and no color was observed, Abe [85] disclosed that, by adding a drop of solution of iodine and potassium iodide to a solution of cellulose obtained by dissolving a filter paper into an aqueous solution of zinc chloride, a deep blue color appeared at once and numerous blue fibers precipitated. This blue color disappeared by warming at about 80°C and reappeared by cooling. The adsorption of molecular iodine onto cellulose fiber was made by adding cellulose fiber into an aqueous solution of I₂/KI in the presence of Na₂SO₄ for 1 h at room temperature [86]. The iodine sorption value (ISV) was determined to be within the range of 140–155 mg/g. Iodine was mostly bound to the amorphous region of the fiber. Also, the iodine uptake was higher for cellulosic fiber with a lower crystallinity extent. Indeed, viscos fibers with the smallest portion of crystalline regions (crystallinity index CrI=0.25) and the highest portion of amorphous regions, were able to adsorb the greatest amount of iodine, and lyocell fibers with the highest crystallinity index (CrI=0.44) adsorbed the smallest amount. Mizrahi and Domb [87] realized complexes of ethylcellulose (EC) and hydroxypropylcellulose (HPC) with iodine, by immersing polymer powder in aqueous I₂/KI solution for 24 h at room temperature. Mucoadhesive tablets were made tested for their antifungal and antibacterial activities to be employed for the treatment of oral infections. The maximum iodine binding capacity was 35.5 and 17.8% for HPC and EC, respectively. Two absorption bands at 210 and 360 nm in the UV-visible spectrum of I₂-EC were observed and assigned to the adduct. It was suggested that iodine molecules most likely resided in the amorphous regions of the EC polymer. The biological assays of adducts were measured for Candida albicans and Porphyromonas gingivalis, in terms of diameter of inhibition zone; for I₂-HPC (35.5% iodine), the diameters were 35.3 and 32.1 mm, respectively, and for I₂-EC (17.8% iodine), they were 33 and 26 mm. Also, the release capacity of iodine from the tablets when immersed into phosphate buffer (pH=6.5) at 37°C was nearly 0.55 and 0.3 mg for I₂-HPC and I₂-EC, respectively, after about 7 h of immersion. Wang and Eastal [88] studied the interaction of EC with iodine by immersing EC membranes in aqueous iodine-iodide solution at room temperature for 24 h. The iodine-doped EC membrane was colored from orange to brown, depending on the iodine concentration. Iodine absorption increased rapidly with iodine concentration, at concentrations lower than about 0.01 mol·l⁻¹. Two UV absorption bands of the iodine-EC membrane at 280 and 350 nm were detected and were assigned to the complexes with I₂ and I₃⁻, respectively. The EC-I₃⁻ complex formation was evidenced by the appearance of a strong absorption band at 138 cm⁻¹ in the far-infrared spectrum of the doped membrane. Thermal analysis suggested that the iodine-doped EC became more crystalline, that is a chain ordering occurrence. The iodinated EC membrane was valorized in the permeability of oxygen and nitrogen, and it was found that the permeability decreased with an increase in the concentration of iodine up to 0.003 mol·l⁻¹ and increased sharply at higher iodine concentrations.

Khare and his co-workers [89] studied the conductivity of the metal-EC-metal sandwich as a function of iodine concentration in the temperature range of 333–383 K, under the electrical field of (3.0–5.5)×10⁴ V/cm. The
conductivity of the sandwich films increased on doping with iodine; the dopant iodine molecules provided links between the polymer molecules in the amorphous region, thus resulting in the formation of CTCs. The electrical conduction followed Ohm’s law at lower fields, while at higher fields, space-charge limited current (SCLC) was observed.

In a continuation of their work on the complexation of polysaccharides with molecular iodine, Yu and Atalla [90] studied the formation of xylan (Figure 2B) and iodine in an aqueous solution comprising xylan, CaCl₂, and I₂/KI. A blue precipitate occurred upon mixing the components. The complex I₂-xylan was very sensitive to iodide concentration, that is, in the absence of KI, two absorption bands in the UV-visible spectrum at 610 and 490 nm (shoulder) were detected and, by increasing the iodide concentration to 5 wt%, the absorption maximum position at 610 nm shifted toward that of 490 nm. Also, the CaCl₂ concentration influenced the complex formation; at concentrations <25%, the complex did not form, as indicated by the absence of color and the absence of absorption bands in the UV-visible spectrum. The electronic spectra indicated three linear polyiodides, I₉³⁻, I₁₁³⁻, and I₁₃³⁻ structures, which were the linear aggregates of the I⁻ and I₅⁻ substructures according to the Raman spectra (two bands at \( \lambda_{\text{max}} = 110 \text{ cm}^{-1} \) and \( \lambda_{\text{max}} = 160 \text{ cm}^{-1} \)).

Also, Morak and Thompson [91], Gaillard [92], Gaillard and Bailey [93] and Gaillard et al. [94] studied the interaction of xylan with iodine and its precipitation in aqueous calcium chloride solutions. The complexation of xylan with iodine occurred in a manner similar to that of amylose, and the blue color also manifested. However, unlike the amylose, the iodine content of the complex from xylan was found to vary with the concentration of the reactants, indicating the absence of a preferred stoichiometry. The precipitation by iodine complexation in aqueous calcium chloride solutions proved to be a convenient way to separate linear polysaccharides from branched ones; linear polysaccharides were precipitated from 1% solution in 30% aqueous calcium chloride solutions, whereas branched polysaccharides were not. In this way, xylan can be isolated.

### 2.1.3 Iodine-chitin/chitosan/alginate complexes

To our dismay, only one report tackled the complexation of iodine with chitin (Figure 3A), as far as our present research has reached. Takahashi [95] disclosed results of the treatment of chitin by I₂/KI solution for 24 h at room temperature. Such treatment gave dark purple stained adducts. The iodine content in the adduct was in the range of 9–20%, depending on the amount of chitin used. Overall, one molecular iodine for 6.4 residues of chitin in the iodine-chitin was estimated.

Unlike chitin, the starting material of chitosan (Figure 3B), chitosan is very prone to form a complex with an iodine molecule. Kato and his co-workers [96] made the iodine-chitosan adduct in the form of black flaky crystals, by dipping chitosan into an I₂/KI aqueous solution overnight at room temperature. The obtained complex released its iodine molecules by evaporation at temperatures >80°C, or by immersion into an aqueous alkali solution. It was claimed that the complex was useful as a deodorant and sterilizer or a disinfectant for drinking water, providing the release of the active iodine with time. Also, a disinfectant fiber could be made by sticking the adduct onto a fiber.

Yajima et al. [97] prepared the I₂-chitosan complex by freezing a mixture of chitosan and I₂/KI solution at -20°C.

![Figure 3](image.png)  
Figure 3 (A) Chitin, (B) chitosan, (C) alginic acid.
and then thawing it at 4°C. The purple-colored complex absorbed at $\lambda_{\text{max}} = 500$ nm, regardless of the iodine/chitosan concentrations and temperature. Its CD spectrum showed two opposite bands at around 500 nm. As with the iodine-amyllose [72, 74], the coloration of the complex was proposed to be the result of a left-handed iodine/iodide dimer exciton-coupled mechanism involving charge-transfer between iodine/iodide and the chitosan chain, and the configuration interaction among the electronic transition states of iodine/iodide. As to its stability, the complex was unstable at room temperature and the purple color started to fade, but it was very stable at temperatures as low as 4°C and for as long as 6 months. A resonance Raman spectrum of its HNO$_3$ solution exhibited two peaks, a stronger one at 110 cm$^{-1}$ and a weaker one at 150 cm$^{-1}$, assigned to the $I_3^-$ symmetric stretching vibration and the $I_5^-$ asymmetric stretching vibration, respectively; these bands were closer to those observed for I$_2$-PVA and I$_2$-amylose. As revealed by the $^{13}$C NMR spectrum of the I$_2$-chitosan, the effect of heavy halogen (iodine) on the chemical shifts ($\delta$) of the carbons of the glucosamine residue was not great; only the chemical shifts of C1, C3 and C4 were displaced to lower fields, but not significantly ($\Delta\delta = 0.1$–0.2 ppm). This finding would suggest that the nitrogen atom was not involved in the binding of iodine as claimed elsewhere [98, 99]. Another important facet of this study was that the coloring phenomenon is believed to be related primarily to $I_3^-$ ions and to the cylindrically-shaped assembly of extended chitosan chains including iodine/iodide molecules.

Hassan [100] invented a pharmaceutical hydrogel, referred to as “ionic chitosan iodine complex, ICIC”, composed of chitosan or a chitosan derivative (molecular weight of 100–800 kDa), an aqueous vehicle (acetic, lactic, citric, or glycolic acid), a polyol [ethylene or propylene glycol, glycerol, sorbitol, or polyethylene glycol (PEG)], molecular iodine, or an iodide ion source (potassium iodide, sodium iodide, or zinc iodide). It was claimed that the gel heals wounds and acts as an antiseptic. The color of the ICIC was dark purple, while that of the I$_2$-chitosan complexes was dark brown or orange yellow.

The effect of iodine on the morphological changes was also applied to the carbonization of chitosan under the same experimental strategy [84]. The iodine content in chitosan after iodine treatment at 120°C for 24 h was about 260 wt%, higher than that for starch. A deep blue color was observed with a change of shape of chitosan film. The char yield of carbonization at 800°C was slightly enhanced upon iodination (by 2 wt%), 33 vs. 31 wt%. Adsorption measurements indicated that the chitosan film and its iodinated one were non-porous materials, as the specific surface areas were found to be <30 m$^2$/g. Raman analysis suggested that the iodine species would have interacted with chitosan in the same way as with cellulose. Also, this analysis implied that the major iodine species was $I_2^-$ (the intensity of the band at 110 cm$^{-1}$ being stronger than that at 169 cm$^{-1}$), which may have reacted with amino groups of chitosan. The amino groups, being outside in the two-helical conformation of the macromolecule, would have made iodine molecules species adsorb physically (physisorption), surrounding the $I_2^-$ species; this fact would explain the higher iodine uptake. The possible partial oxidation of chitosan by molecular iodine was mentioned, leading to low stabilization.

A few reports on the iodine treatment of alginate were provided by the literature. Takahashi [95, 101] prepared iodine-alginate complexes by immersing the metal-alginate (metal: sodium, cadmium or calcium; the ratio of D-mannuronate/ L-guluronate G/M: 091; degree of polymerization: 468–473) into an I/KI aqueous solution for 24 h at room temperature. Addition of acid to the mixture gave a blue color. Films from the iodine-metal alginate were formed. The blue color intensity varied as a function of pH and reached a maximum at pH = 1. The amounts of complexes increased with immersing time and attained highest values after 20 h, and the complexes formation tended to be inhibited by increasing the amount of KI. Algic acid (Figure 3C) was found to uptake iodine molecules and the amount of complexed iodine was estimated by the ratio of sugar residue over the moles of iodine; it was approximately 12–15. The iodine uptake decreased by increasing the KI concentration. The binding capacity of alginic acid to iodine was similar to that of chitin.

### 2.1.4 Iodine-glycogen complex

Glycogen, a polysaccharide found in animals, is sometimes termed “animal starch”, being similar to amyllopectin in structure (Figure 4). It is mostly stored in muscles, liver and red blood cells. Like starch, glycogen also interacts with molecular iodine to afford a deep reddish-brown complex. The iodine-glycogen complex is absorbed at $\lambda_{\text{max}} = 395$ nm [102]. Such a complex, with its characteristic color, was exploited to ascertain glycogen quantitatively [103, 104]. However, Morris [105] proved that the method based on this color formation, for determining glycogen content, was not satisfactory, because the intensity of this color varies not only with glycogen concentration but also with the temperature, the concentration of iodine, and the glycogen source. Kumari et al. [106, 107] and Lecker et al. [108] undertook a detailed study on the iodine-glycogen complex.
The heat of formation of the complex was estimated to be nearly -40 kJ/mol. The iodine binding capacity of the complex, calculated as the maximum mass of bound iodine over the total mass of the complex, was 0.3% (w/w) at 3°C. A series of UV absorption bands of the complex were detected at 408, 453, 496, 560, 650, and 698 nm. The bands at 408, 453, 560, and 650 nm were comparable with those of iodine-amylopectin (412, 458, 550, and 640 nm), and the bands at 496 and 698 nm were assigned to a kind of the species I\(_4\). The bands at 453 and 560 nm were more conspicuous at higher iodine concentrations. About 12.5% of the mass of glycogen took part in the iodine-glycogen complex formation, indicating the involvement of four iodine atoms for every 25 anhydroglucose units (AGU). Also, since the chromophore was due to the I\(_4\) unit within the helix of 11 AGUs, only 44% of the AGUs (11/25) were thought to be involved in the complex formation. These results suggested a strong similarity between the iodine-glycogen and the iodine-amylopectin structures, as stated above.

The influence of calcium chloride on the iodine-glycogen complex was the intensification of such complexation, destabilization of the helical geometry imposed by such binding, and a loss of dichroism [109]. Dreiling et al. [110] observed that the mixture of glycogen solution in 7–10% perchloric acid with I\(_2\)/KI solution containing saturated CaCl\(_2\) and in the presence of bovine enzyme was amber-brown and absorbed at 460 nm. Such color appeared instantaneously, was stable for up to 2 h, and was linear with respect to glycogen concentrations up to 600 \(\mu\)g glycogen/ml.

### 2.1.5 Iodine-proteinic fiber complexes

Natural silk fibroin (Figure 5) belongs to fibrillar proteins and has a molecular weight in the region of 370,000 Da and a macrochain length of about 150 nm. *Bombyx mori* (*B. Mori*, silkworms) silk fibroin is composed of no <16 amino acids, of which glycine (--43 mol%), alanine (--30 mol%), serine (--12 mol%), tyrosine (--5 mol%) are the predominant ones [111–113], corresponding to the primary structure consisting of a six-unit repeating unit: (Gly-Ala-Gly-Ala-Gly-Ser)_n. Its macrostructure consists of anti-parallel pleated β-sheets, with a huge number of inter-chain hydrogen bonds, responsible for its crystallinity.

It is known that several amino-acids developed adducts with molecular iodine [114], claimed to be used in the production of feedstuff, food additives, disinfectants, antiseptics and medication. Shao and his co-workers [115] treated a degummed and UV/ozone irradiated *B. mori* silk fiber with saturated iodine ethanolic solution in the dark at 22°C for 24 h. The content of iodine was about 5% in the bulk iodinated silk and 0.9% on the surface. Khan et al. [116] reported a process of making carbon fiber from *B. mori* silk fibroin after iodine treatment. The silk fibroin was exposed to iodine vapors at 100°C for varying periods of time, after which the fiber color turned to dark brown. The iodine sorption extent by the silk reached about 52 wt% after 24 h of exposure. A Raman spectrum of iodinated silk fiber showed two strong peaks at 112 and 168 cm\(^{-1}\), which were attributed to the I\(_3^-\) and I\(_5^-\) vibrations, respectively. The I\(_2\)/silk complex was carbonized at 800°C under argon ambiance. The carbonization yield depended on the iodine content; that is, while it was only 29 wt% from untreated silk, the carbonization yield increased to 36 wt% as a function of iodine treatment for 12 h, and beyond this time, it decreased gradually. The effect of
iodine treatment on the properties of the carbon fibers was conspicuous as the ensued mechanical properties were different; the average values of strength and elongation of carbon fibers prepared from I₂-silk fiber were 12.6 gf and 0.7 mm, respectively, versus 8.2 gf and 0.5 mm for carbon fibers prepared from untreated fiber. However, both carbon fibers showed a lack of crystallinity as suggested by wide angle X-ray diffraction (WAXD) spectra, one peak at 2θ = 24°. For both carbon fibers, two broad peaks, one at 1369 cm⁻¹ for D band (disorder peak) and another at 1589 cm⁻¹ for G band (graphite peak), respectively, were seen in their Raman spectra. The patterns of these spectra samples were similar to a pattern of diamond-like carbon (DLC), where a mixture of sp² and sp³ carbons existed. In another report, however, the authors [117] found that both untreated and iodinated silk fibroin (SF) fiber exhibited an amorphous structure when carbonized to 1200°C and, after being carbonized at 1400°C for 12 h, a graphite-like structure was obtained and the graphite layers of SF fibers became more ordered after iodine treatment.

Under identical conditions and in the same line of investigation as in [116], Kahn et al. [118] studied the carbon formation from Antheraea pernyi silk fibroin fiber. The composition of the latter silk is different from that of B. mori silk, having predominantly alanine (Ala), aspartic acid (Asp), and arginine (Arg) amino acid residues. The uptake of iodine by this silk fibroin fiber reached 46 and 57 wt% after 12 and 24 h of exposure to iodine vapors, respectively. Thermal treatment of the iodinated silk at temperatures >270°C produced a greater stiffness (higher storage modulus) and restricted the melting flow of the fiber, a result of an intermolecular crosslinking. The carbon yield from iodinated silk at 800°C was greater than that from the untreated one, 39% vs. 29% after 12 h. Carbon fibers obtained from both untreated and iodinated treated silk fibroin fiber, particularly the treated one, were of a homogenous structure. The carbon fiber from iodinated silk fiber showed an amorphous structure, as revealed by a broad peak at 2θ = 24° in the WAXD profile; the crystalline structure of the untreated silk fiber appeared at 16.6° and 20.1°. Upon heating the I₂-silk fiber from room temperature to 800°C, the two peaks disappeared gradually and the peak at 24° appeared with increasing intensity. Raman spectra of the carbon fibers formed from the iodinated material and the non-iodinated one at 800°C showed two bands, the G and D bands, at 1577 and 1567 cm⁻¹, and 1350 and 1349 cm⁻¹, respectively. As to the mechanical properties of the carbon fibers obtained, the ultimate tensile strength and the toughness were 14 MPa and 36 J/kg for the untreated one and were 18 MPa and 67 J/kg for the iodinated one; the iodine treatment induced an increase of the mechanical properties of the carbon fiber from A. pernyi silk fibroin.

In other works, Khan et al. [119, 120] treated B. mori silk fibroin by immersion in I₂/KI aqueous solution for various periods at room temperature. The maximum sorption of the iodine by the silk fibroin fiber was measured as 20 wt% after 40 h of immersion. Polyiodide ions I⁻ and I₃⁻ were claimed to be formed as indicated by Raman spectra. Also, the iodine treatment brought some changes in the fine structure of the fiber, as suggested by Fourier transform infrared spectroscopy (FTIR) analysis; the absorption band of the amide at 1653 cm⁻¹, assigned to a β-sheet conformation, shifted gradually to 1647, 1632, and 1628 cm⁻¹ with an increase in the absorbed iodine content (8, 15, and 20 wt%). The different analyses suggested that polyiodide ions were inserted in the amorphous region of the silk fibroin. Iodine treatment seemed to weaken the hydrogen bonding of the β-sheet structure of the fiber. Heating the iodinated silk fibroin above 270°C induced crosslinking of the fiber, and its melt flow was inhibited.

As for the wool and its reaction with molecular iodine, literature provides reports of Stromeyer, which date back to 1815; this author mentioned that wool and silk (nitrogenous substances) with iodine gave yellow colors upon exposure to iodine. Being a fibrous protein, its complex chemical structure consisted of peptide linkages (Figure 6) having higher contents of tyrosine and glycine residues; the macromolecular chains are disposed in a helical geometry (α-helix structure). Richards and Speakman [121, 122] treated wool with aqueous solutions of iodine in potassium iodide at different pH values and temperatures. The extent of iodine incorporation into the tyrosine unit was medium-dependent. In aqueous solutions, the uptake extent was limited to 75% under the best conditions (64 h at 22.2°C and pH 9). In methanolic and ethanolic solutions, the iodination extent was about 96%, and the tyrosine was converted into 3,5-diiodotyrosine in 72 h at 22.2°C. The fact that tyrosine was exclusively iodinated could be used as a means for assessing its distribution along the length of single fibers, by taking radiographs after the fibers have been iodinated with ¹²⁵I. In another work [123], the iodination extent was studied as a function of the alcohol length, and it was found that with n-propanol, n-butanol, and n-pentanol, the iodination extent was low, suggesting that the fine structure of wool is inaccessible to molecules larger than those of n-propanol.

In Crewther and Dowling’s works [124–126], wool was attacked by molecular iodine in a variety of media including ethanol, propanol, acetone, CCl₄, CH₂Cl₂, and in aqueous solutions of KI. The contact was allowed for a range of time of 0.25 to 15 days at room temperature,
and the rapid reaction of iodine with wool in aqueous media was noticed. The effects of iodination were the oxidation of disulfide (S-S-) and sulfhydryl (S-H) linkages and the tyrosine content. In all media, oxidation of the most disulfide and sulfhydryl groups took place. Crewther observed the phenomenon of medium-dependent iodination extent and that iodination of wool fibers in ethanol or n-propanol accelerated the first stage and retarded the second one. To clear up such a fact, the rate and the extent of the reaction of N-acetyltyrosine ethyl ester with iodine, using ethanol, n-propanol, and n-butanol as solvents, were studied. The extent of tyrosine iodination was in this order of alcohol: ethanol > n-propanol > n-butanol. Addition of traces of water to the anhydrous alcohol solvents increased both the rate and the iodination extent, and the addition of anhydrous NaOH to the anhydrous alcohols caused marginal increases in iodination.

Albumin, a water-soluble protein that occurs in nearly all animal tissue, bacteria, and certain plant matter, was found to bind iodine, and such iodine-albumin complexes showed distinct disinfecting capacity and preservation of biologicals [37, 127]; the fixation of molecular iodine onto albumin was achieved by passing a solution of albumin through a bed or column of a solid, insoluble source. In its application as a disinfectant, two binding sites of albumin were thought to manifest: one binds iodine covalently, and the other holds it reversibly (apparently on the surface of the albumin). These sites will release iodine for reaction with microbes. Iodine-albumin is a reagent for the determination of plasma volume [128]. Reaction of iodine with egg albumin was earlier reported [129].

Amyloid is defined as an unbranched protein fiber whose repeating substructure consists of β-strands that run perpendicular to the fiber axis, forming a cross-β-sheet of indefinite length [130]. Amyloid fibrils are associated with diseases such as Alzheimer’s and Parkinson’s diseases and others [42]. Amyloid becomes blue when treated with molecular iodine. The blue violaceous reaction of amyloid with iodine in the presence of sulfuric acid dates back to 1980s, and its history was elegantly penned by Aterman [131]. The term “amyloid” has been long mistakenly taken as synonymous to “starch-like” as pointed out by this author. Dzwolak [132] described the complex formation when insulin amyloid fibril was incubated in the presence of molecular iodine potassium iodide solution at 37°C. The observed violet color strongly indicated the formation of an inclusion complex between the amyloid fibrils and iodine; the complex was stable up to 90°C. The effect of such treatment was the shifting of the IR absorption band at 1654 cm⁻¹, a characteristic band of native α-helices, to 1625 cm⁻¹, a characteristic band of stacked β-strands. The UV-visible analysis revealed the appearance of a new band at 495 nm. The intensities of the bands 1625 cm⁻¹ (IR) and 495 nm (UV-visible) increased with incubating time. Overall, the iodine amyloid provided a probe of void volumes in protein fibrils.

### 2.2 Iodine-synthetic polymers complexes

#### 2.2.1 Iodine-poly(vinyl acetate)/poly(vinyl alcohol) complexes

In 1973, Pritchard and Serra [133] reported the complexation of poly(vinyl acetate) (PVAc) (Figure 7A) with iodine. In their work, methanolic PVAc (molecular weight=5×10⁴–5×10⁵) solution was mixed with methanolic iodine and
The formation of such a complex required coordination by water, and the orientation of several polymer segments around each iodine unit. However, the degree of extension of the polymer chain had a minor influence on the formation of the complex. Two UV-visible absorbance bands of the complex were observed at 520 and 510 nm. The color of I2-PVAc complex was independent of the method of preparation and polymerization degree of 1000 would be as efficient as the conventional starch in iodometry. Yet, the cause of this blue color has been a puzzle for a long time. As explained, these could be due to different types and numbers of cyclic acetics and ketal structures within the PVA chains. The iodination promoted crystal lattice change, that is, the formation of two complexes, one in the amorphous region (λ_{max}=470 nm) and the other in the crystalline region (λ_{max}=580 nm), which explained the color change to red-violet. As explained, these could be due to the formation of two complexes, one in the amorphous region (λ_{max}=580 nm) and the other in the crystalline region (λ_{max}=470 nm); this would suggest that the iodination penetration will cause the formation of a co-crystal with the PVA chain. Upon iodine desorption, the absorption band at λ_{max}=470 nm disappeared faster than that at λ_{max}=580 nm.

Pritchard and Akintola [146] studied the effect of residual acetate groups in PVA on the color formation of the mixture of PVA-boric acid-iodine. The color was dark yellow-green to dark-blue for PVA with 0.5% residual acetate groups, and dark yellow-green to deep violet-blue for PVA with 12% residual acetate groups, depending on the PVA concentration. However, the colors were pale yellow and rose-wine, respectively, in the absence of boric acid. In the latter case, the development of the blue to green color characterized by λ_{max}=620 nm was slow, even at higher concentrations of a well-hydrolyzed PVA and of aqueous iodine and KI. By contrast, the presence of sufficient boric acid annihilated the dependence of the blue color formation on the time and the tacticity of PVA [144]. Only I^{-} was thought to exist in the blue-colored complex, that is the occurrence of I^{-}, I_{3}^{-}, and I_{5}^{-} was unlikely. The blue color of the I2-PVA complex, in the absence of boric acid, was believed to arise probably from different types and numbers of cyclic acetics and ketal structures within the PVA chains. The X-ray studies of Choi and Miyasaka [147] on the lightly iodinated PVA, in which the complexation occurred mostly in the amorphous region, indicated that a series of peaks with a periodicity of 3.1 Å appeared in a much longer distance than that due to I_{3}^{-} and I_{5}^{-}, suggesting that these iodides were actually located in zones where they interfered with each other. In another place, Choi et al. [148] investigated the sorption of iodine by PVA by soaking the polymer with I_{2}/KI solutions for 24 h at 20°C. Their findings were that the sorption fitted Freundlich isotherm over a range of iodine concentration from 5×10^{-3} to 6×10^{-1} mol·l^{-1}, and that both crystalline and amorphous regions were iodinated. Also, the iodination promoted crystal lattice change, that is, one PVA chain of a hydrogen-bonded pair in the virgin polymer cell was substituted with a polyiodine chain, and increased its drawability as clearly observed in the stress-strain measurements. In a continuing work, Sakuramachi et al. [149] showed the behavior of the I2-PVA complex (a PVA film) at high iodine concentrations, and upon formalization of the polymer. At a concentration of iodine of 5×10^{-1} mol·l^{-1}, a blue complex was detected at λ_{max}=580 nm, and at concentrations of higher than 5×10^{-2} mol·l^{-1}, another band at λ_{max}=470 nm appeared, which explained the color change to red-violet. As explained, these could be due to the formation of two complexes, one in the amorphous region (λ_{max}=580 nm) and the other in the crystalline region (λ_{max}=470 nm); this would suggest that the iodination penetration will cause the formation of a co-crystal with the PVA chain. Upon iodine desorption, the absorption band at λ_{max}=470 nm disappeared faster than that at λ_{max}=580 nm.

**Figure 7** (A) Poly(vinyl acetate) (PVAc), (B) poly(vinyl alcohol) (PVA).
The color shift from blue to red-violet was seen even for low iodine concentrations when PVA was formalized (generating a formal linkage). In addition, the complex in the amorphous region was found to be stable in formalized PVA. Later, Choi and Miyasaka [150] observed that the Raman spectra of the lightly and heavily iodinated PVA in its crystal phase showed the two peaks of $I_3^-$ species at 109 and 161 cm$^{-1}$. The former peak was much stronger than the latter one in a heavily iodinated specimen, whereas the former peak was comparable with the latter one in a lightly iodinated sample. The average iodine-iodine distance was 3.2 Å, which is different from 3.08 Å of the I$_5^-$ of the I$_5^-\bar{\text{I}}$ complex formed in the amorphous phase. Also, the peak in the hydrogen-bonding state in the crystal phase occurred upon complex formation, as evidenced by IR and NMR analyses.

From the $^{125}$I emission Mössbauer measurements performed on unidirectionally stretched I$_2$-PVA polarizing, iodine was observed to be in the form of linear polyiodides, $I^-_2$ and $I^-_3$, lying parallel to the stretch direction of the PVA films [152].

The complexation of iodine by PVA and the blue color produced were employed as a useful method for the quantitative determination of PVA in systems, by means of a calibration curve using $\lambda_{max}=495$ nm, a characteristic absorption band of $I_2^-$. For example, the amount of PVA adsorbed on the oil globules in liquid paraffin oil-water emulsions prepared by the polymer could be estimated by iodination [153].

Lyoo et al. [154] devised a method for the determination of desorbed iodine from the high molecular weight syndiotactic s-I$_2$-PVA complex, involving the weight loss of s-PVA/iodine film and the solubility of s-PVA film after immersion in hot water; in the case of the atactic a-PVA film, the iodine desorption was almost 100%, because a-PVA was readily soluble in water. At an immersion temperature of 80°C and for 1 min soaking time, the desorption extent of iodine from s-I$_2$-PVA complex was near 13%; at this working temperature, the solubility of s-PVA film in water was low, not exceeding 3.5%. By increasing the drawing temperature and the draw ratio, the iodine desorption was suppressed significantly (down to 5–6%).

Han and Lyoo [155] showed the impacts of the syndiotacticity and the molecular weight of PVA on the durability of the I$_2$-PVA complex in warm and humid conditions (relative humidity of 80% and temperature of 50°C). Such parameters are important for polarizing films. The change of the polarizing efficiency of the I$_2$-PVA complex films having $M_n$ of 4000 and with syndiotacticity of 56% and 59%, in warm and humid conditions, was almost zero, whereas those of the I$_2$-PVA film with syndiotacticity of 53% and with $M_n$ values of 1700 and 4000 were about 60% and 50%, respectively, under the same conditions. Han et al. [156] also extended such a study to the recycled I$_2$-PVA complex film. The results indicated that the recycled I$_2$-PVA polarizing film showed effective transmittance and polarizing efficiency values comparable with those of commercial I$_2$-PVA polarizing film.

Naorem and Singh [157] reported the influence of sodium dodecyl sulfate (SDS), an anionic surfactant, and $n$-propanol on the stability of I$_2$-PVA, I$_2$-PVP, and I$_2$-HPC prepared with I$_2$/KI aqueous solutions. The absorption band at 495 nm, attributed to $I_2^-$ present in I$_2$-PVA, disappeared upon addition of SDS solution, indicating the disruption of the complex. SDS molecules would have acted to restore the intermolecular hydrogen bonding within the PVA chains. Also, the presence of $n$-propanol favored the breakdown of this complex for the same reason. On the contrary, low SDS concentrations and $n$-propanol were found to even improve the I$_2$-PVP and I$_2$-HPC complexes.

One of the state-of-the-art application domains of the I$_2$-PVA complex is in liquid crystal display (LCD) panels as a polarizer, due to the one-dimensional alignment of polyiodide ions with the oriented PVA chains, resulting in an excellent dichromatic performance [158]. Kalayjian et al. [159] valorized I$_2$-PVA as a polarizer in contrast retina, taking advantage of the linear alignment of polyiodide ions $I_n^-$ with the PVA chains. The recycling of used PVA from LCD waste is of a great value. In view of reuse, expanded PVAs are well suited as support material for enzyme immobilization, tissue scaffolds and drug delivery systems, which required high surface areas. In this line, Hunt et al. [160] applied the expansion technique to PVA and found that the addition of iodine enhanced substantially its surface area up to 143.1 m$^2$g$^{-1}$ (that of virgin PVA was lower than 1 m$^2$g$^{-1}$). The expansion of polarizing the I$_2$-PVA film resulted in a surface area of 95.0 m$^2$g$^{-1}$, showing clearly the effect of iodine doping.

Chetri et al. [161] investigated the impact of temperature on the electrical conductivity of the I$_2$-PVA complex membrane made by immersing a thin PVA film into I$_2$/KI aqueous solution. The conductivity of the complex membrane increased from 150°C to 170°C, stabilized at 180°C, dropped from 200°C to 240°C, and finally leveled off at 250°C. The conductivity increase was reasoned in terms of polyelectrolyte formation upon heating at high temperatures, resulting from elimination of HI and HOI as confirmed by IR spectroscopy analysis. The suggested mechanism for iodine-induced dehydration is depicted in Scheme 1.
I₂-PVA with 90% of iodine, prepared by heating a mixture of PVA film with iodine in an evacuated and sealed ampoule, showed an electrical conductivity of \( \sigma = 1.5 \times 10^{-2} \text{ S cm}^{-1} \) [162].

A great effort has been expended by Yang and Horii [163] in resolving the microstructures of the I₂-PVA complex hydrogels, using high resolution \(^{13}\text{C}\) NMR spectroscopy; the studied hydrogels with an [OH]/[I₂] molar ratio of 76.7 were prepared from concentrated solutions (PVA-I₂/KI). On preparing such hydrogels, the following color changes were observed on cooling from 120°C to room temperature: yellow, greenish-yellow, green, bluish green, and finally dark blue, which corresponds to the color characteristic of stable I₂-PVA complex. The outcome of this research was that these hydrogels contained 60% of one highly mobile component and one broader one. The first one was assigned to the soluble or highly water-swollen uncomplexed PVA chains, and the second one was ascribed to the aggregated PVA chains involved in the formation of the iodine-PVA complexes.

Iodination of PVA is a critical step to making carbon fiber from this polymer [164]. I₂-PVA was made by treating PVA fiber with a diameter of about 110 μm with an aqueous solution of I₂-NH₄I solution for 2 h at 90°C. Iodination promoted the formation of polyene domains within the PVA structure via a dehydration reaction, favoring a carbonization process; the polyene sequences were confirmed by the appearance of two strong peaks at around 1120 cm⁻¹ and 1500 cm⁻¹ in the Raman spectrum [besides those for polyiodide ions 160 cm⁻¹ (I₃⁻), 217 cm⁻¹ (I⁻), 320 cm⁻¹ (I₂⁻)]. The fiber was then stabilized by heat treatment at 200°C in air, providing insolubilization of the adduct. The stabilized I₂-PVA was carbonized at 800°C under inert atmosphere to form hollow carbon fiber (H-CF). WAXD measurement of H-CF revealed two broad peaks at around \( 2 \theta = 18-24^\circ \) and \( 2 \theta = 42-45^\circ \), characteristic peaks of graphite, and its Raman spectrum revealed two prominent peaks, the D and G bands, at 1344 cm⁻¹ and 1586 cm⁻¹, respectively. In another work, Jalal Uddin et al. [165] demonstrated the enhancement effect of iodine doping on the mechanical properties of gel-spun PVA fiber. A color change of I₂-PVA was observed during the gel spinning preparation on going from reddish to dark purple, indicating the interaction of PVA with iodine. The mechanical properties of drawn gel-spun PVA fiber were generally superior to those of virgin PVA as follows: 2.2 vs. 1.6 GPa (tensile strength), 47 vs. 34 GPa (initial modulus), 84 MPa vs. 62 MPa (toughness), and 74 vs. 74% (elongation at break). Also, the presence of iodine improved other properties such as the density, the crystallinity, and the birefringence of the drawn PVA fiber, as follows: 1.3214 vs. 1.3184 g·cm⁻³ (density), 69 vs. 65% (crystallinity extent), 52\( \times 10^{-3} \) vs. 49\( \times 10^{-3} \) (birefringence).

Carbon fibers were also made from electrospun PVA nanofibers with the aid of iodination [166]. The carbonization at 1200°C of nanofibers iodinated with saturated I₂ vapors at 80°C for 24 h led to a graphitic material with a good carbon yield of 21%. The conversion was believed to involve dehydration of PVA, as shown in Scheme 2; iodine acted as a catalyst for dehydration of alcohols. The carbon nanofibers obtained were smaller than the I₂-PVA precursor, i.e. the average diameter of the former was 4.1\( \times 10^2 \) nm against 5.3\( \times 10^2 \) nm for the latter. The work presented by Bin et al. [167] supported further the benefits of iodine doping on the carbonization success of PVA.

Shin et al. [168–171] and Woo et al. [172] embarked on the study of the structure and processability of iodination products of oriented and unoriented PVA using I₂/KI solution at room temperature for 24 h. The crystallinity

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**Scheme 1** Mechanism of the iodine-induced dehydration of poly(vinyl alcohol) (PVA).

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**Scheme 2** Carbonization of I₂-poly(vinyl alcohol) (I₂-PVA) nanofibers.
of oriented and unoriented PVA subjected to iodination was 21.3% and 37.0%, respectively. The weight gains and molar ratios of the oriented and oriented films increased rapidly with I$_2$/KI concentration to 1.0 mol/l and 0.5 mol/l, respectively. Thermal analyses indicated that the amount of I$_3^-$ ions increased with increasing I$_2$/KI up to 65% of weight gain, above which the increase rate dropped and the amount of I$_5^-$ ions from the I$_3^-$ ions increased. The differential scanning calorimetry (DSC) thermogram of I$_2$-PVA films revealed two peaks at 145°C and 160–170°C, attributable to the melting of crystals and the glass transition temperature $T_g$ of undrawn films showed that iodination affected both the glass transition temperature $T_g$ and the $\alpha$-relaxation temperature $T_{\alpha}$ of PVA; their decrease from 70°C to 60°C, and 150°C to 100–130°C, respectively. This finding was rationalized in terms of iodine-induced breaking of intermolecular hydrogen bonds in amorphous and crystalline regions of PVA. This reasoning was also valid for the lower mechanical properties of I$_2$-PVA (yield point and tensile strength) compared to those of untreated PVA. In general, these properties were enhanced with decreasing concentration of iodinating solution (I$_2$/KI) and on lowering the draw temperature from 90°C downward. On the contrary, their strains were observed to increase with increasing I$_2$/KI concentration and draw temperature up to 90°C. Also, the maximum draw ratios (MDR) of I$_2$-PVA films were generally higher than that of the untreated film and increased with I$_2$/KI concentration up to 2 mol/l, suggesting the positive effect of iodination on the draw ratio of PVA. Another fact was that the greater the MDR (up to a value for I$_2$/KI concentration of 2 mol/l) was, the higher the heat of fusion ($\Delta H$) of the de-iodinated film and its degree of crystallinity (%Crys) were and the lower its melting temperature ($T_m$) was. For example, for an MDR of 0.8 (I$_2$/KI, 0.1 mol/l), $\Delta H$, %Crys, and $T_m$ were 58.83 J/g, 37.94%, 231.44°C, respectively, and for an MDR of 11 (I$_2$/KI, 1.0 mol/l), the corresponding values were 77.89 J/g, 4.987%, and 225.56°C, respectively.

One of the additives to the I$_2$-PVA complex is boric acid, which brought up some changes of the properties of the complex. Boric acid improved the bluish color of the complex, and the intensity of this color increases with its concentration. High amounts of solvents such as acetone, DMF, methanol, ethanol, pyridine, or formic acid, will destroy the complex and the color will fade. Shin et al. [173, 174] reported the use of boric acid treatment to form I$_2$-PVA polarizing film characterized by its transmittance and polarization degree. The acid promoted the formation of iodide species I$_3^-$ and I$_5^-$, and improved the durability of the film under heat and humidity. Boric acid seemed to disfavor the crystallization, inducing the formation of an amorphous region [173]. In fact, Woo et al. [172] worked on the effect of boric acid on the crystallinity and the drawability of the I$_2$-PVA films made by iodinating the PVA solution before and after casting its solution, BC and AC, respectively. No change in the crystallinity for the films AC was found, because boric acid could not permeate into the crystal region of the PVA film prior to the boric acid treatment, and the crystallization of the films BC was prevented, as boric acid may form intramolecular crosslinks on the PVA chain to accelerate the formation of the PVA-iodine complex evenly in the solution state. The MDR, a measure of film drawability, of both types of films BC and AC, decreased with increasing boric acid concentration. The decrease in the drawability of the film BC was believed to be due to intramolecular and intermolecular crosslinking types on the PVA chain segment. Also, that for film AC may be due to the intramolecular crosslinking type, reducing the number of hydroxyl groups on the PVA chains.

Earlier, Zwick [175] experimentally demonstrated that at full iodine saturation of the PVA, 12 vinyl alcohol residues supported by one boric acid molecule form a single turn of a helix which entrapped one iodine atom, out of a long polyoiodide chain nested in the interior of a PVA helix.

Kaneko et al. [176] doped an amylose-grafted PVA film made via a chemoenzymatic pathway (Figure 8), with iodine by soaking the film in KI/I$_2$ ethanol solution. The red-purple complex formed showed UV-visible absorption bands at 300 nm and 570 nm, attributable to the polyiodides I$_3^-$ and I$_5^-$, respectively. The complex was stable for as long as 24 h, inferring insertion of iodide ions within the cavities of the amylose graft chains in this film. However, most of the iodine was desorbed from the PVA film after 24 h.

Sengwa and Kaur [177] showed the effect of iodine doping of PVA film on its dielectric properties. The values of dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were...
found to vary anomalously with iodine concentration increase. Also, there was anomalous variation in the conductivity of the iodine-doped PVA film with increasing iodine concentration. The variations in crystalline and complex formation of PVA molecules with iodine were responsible for the change in the dielectric parameters.

Sengupta et al. [187] studied the effect of pressure (up to 80 kbar) on the Raman vibrational modes of polyiodides in the I₂-PVA complex. In general, higher pressure was found to broaden the Raman bands, arising from distortion of the iodine chains. The band at 107 cm⁻¹ of \( \text{I}_5^- \) shifted fairly rapidly and increased in intensity with pressure, however, the band at 154 cm⁻¹ of \( \text{I}_3^- \) shifted very weakly and diminished in intensity. This intensity, diminishing for the latter polyiodide and increasing for the former, was attributed to the collapse of \( \text{I}_5^- \) into \( \text{I}_2 \) and \( \text{I}_3^- \) at high pressure.

Yokota and Kimura [179] measured the absorption bands of solution containing PVA-I₂-boric acid and found four bands at 650 nm (band D), 226 nm (band A), 290 nm (band B), and 355 nm (band C) attributed to the chromophores \( \text{I}_5^- \), \( \text{I}^- \cdot \text{I}_3^- \), and to \( \text{I}_3^- \cdot \text{I}_2 \), respectively. While the intensity of the band D increased linearly with PVA concentration, those of bands A and B decreased, and that of the band C remained unchanged. Repeated extraction of molecular iodine with CCl₄ from the solutions was accompanied with a gradual decay of the absorbance of \( \text{I}_5^- \).

Sashio and Tanaka [180] observed a two-stage color change on heating I₂-PVA membrane of 10 μm thickness, made by casting a 2 wt% PVA solution over a silica plate, dried under reduced pressure, and then dipped into a I₂/KI solution saturated with potassium sulfate for 5 h at 20°C. Upon heating treatment at 160°C, the blue color of the complex turned yellow and then changed to deep-brown.

Lyoo et al. [181] iodinated PVA microfibril obtained by saponification of poly(vinyl pivalate). Iodine adsorption decreased with increasing drawing temperature, which was explained by an increase in the regularities of PVA microfibrils by drawing. The iodination of PVA microfibril induced a decrease of melting point \( T_m \) of about 100°C, from 260°C to 150–180°C, depending on the drawing temperature. Also, Lee and Lyoo [182] iodinated PVA microspheres (skin/core types) obtained by saponification of the surface of monodisperse PVAc microspheres (diameter =500–1000 μm), by immersing the polymer into I₂/KI aqueous solution. A blue color of the complex, assigned to the presence of \( \text{I}_5^- \), was developed in the case of PVA with high degrees of saponification. The formed complexes were appreciated as useful materials for clinical treatment of vascular diseases.

### 2.2.2 Iodine-nitrogen-containing polymers

#### 2.2.2.1 Iodine-poly(vinylpyrrolidone) complexes

Poly(vinylpyrrolidone) (povidone or PVP) is ranked among the earlier polymers that form a complex with molecular iodine. The I₂-PVP complex (Figure 9) has been distinctly featured with disinfecting properties, and us known under various trade names such as Betadine. The complex reduced, largely, the drawbacks of iodine aqueous solution, namely the irritation and toxicity. In addition, PVP enhances the iodine solubility in water; at 25°C, iodine is soluble in water to the extent of only 0.034%, whereas it is soluble to the extent of 0.58% in 1% aqueous PVP solution, that is, a 17-fold increase [183]. The characteristic absorbance of I₂-PVP complex is \( \lambda_{\text{max}} = 361 \) nm. The iodine molecule is adhered to the PVP matrix through the hydrogen bridge involving the carbonyl groups of the polymers as shown in Figure 9.

Bhagat et al. [184] disclosed the making of membranes that contained PVP in their integrity. This was achieved by UV-grafting of I-vinyl-2-pyrrolidone in the pores of a microporous poly(propylene) host membrane, to form a grafted membrane (PVP-g-PP), and by physical immobilization of preformed PVP in a plasticized cellulose triacetate (CTA) matrix to form the polymer inclusion membrane (PVP-PIM). The former membrane was hydrophilic, with a water uptake capacity of 166 wt%, and the latter one was hydrophobic with a water uptake capacity of only 2 wt%. These membranes were evaluated as means for iodine preconcentration and estimation in aqueous solutions, using the characteristic absorbance of I₂-PVP complex (\( \lambda_{\text{max}} = 361 \) nm).

Guzenko et al. [185] studied the adsorption of molecular iodine on the surface of silica (aerosil A-300, \( S_{\text{sp}} = 300 \) m²/g) modified by PVP; sorption of iodine by silica was weak (0.10–0.12 mmol·g⁻¹). It was claimed that modification of the silica surface by water-soluble polymers provides medical sorbents with new physicochemical properties. The adsorption capacity increased largely with PVP-modified silica; at a PVP content of 100 mg/g in silica, iodine was sorbed in an amount of 0.10–0.12 mmol·g⁻¹.
amount >0.4 mmol·g⁻¹, and the higher the PVP content, the greater the iodine adsorption. According to the UV-visible spectrum of the I₂-PVP/silica, the interaction of iodine with PVP differs from that in I₂-PVP, as suggested by the structure in Figure 10, where the PVP molecules are held to the silica surface via hydrogen bonds with silanol groups. Infrared spectroscopy analysis revealed that for PVP content on the silica surface of 50 mg/g, about 80% of the polymer chains interacted with silanol groups, and 50% when the content was 100 mg/g. The two absorption UV bands of I₂-PVP/silica appeared at 300 nm and 370 nm, whereas those of I₂-PVP were 310 nm and 395 nm.

To make safer plastic items for delivery systems for drugs, nutrients, specimen containers, and surgical devices, Urian [186] combined I₂-PVP with a suitable polymer such as Carbowax 8000 (PEG), ethylene vinyl acetate (EVA) copolymer and ethylene-methacrylate (EMA) copolymer. The materials made from different compositions were tested for their antimicrobial activities and their mechanical properties.

Khan et al. [187] devised an iodine carrier consisting of a PVP-polyurethane block copolymer (PVP-b-PU). Radical copolymerization of N-vinylpyrrolidone with a hydroxyl-containing monomer such as allylic alcohol in the presence of 2,2′-azobisisobutyronitrile (AIBN) as initiator, followed by reaction with a diisocyanate compound [4,4′-diphenylmethane diisocyanate (MDI); toluene diisocyanate (TDI)] led to the conceived PVP-PU copolymer. The latter material was mixed with iodine for 24 h to afford the I₂-PVP/PU complex, readily usable for coating a medical device.

Water-resistant nanofibers with an average diameter of 150–640 nm for wood dressings were made by electrospinning of PVP and PVP/PEG followed by crosslinking with 4,4′-diazidostilbene-2,2′-disulfonic acid disodium salt (DAS) and then complexation with iodine [188]. The electrical conductivities σ for the different complexes were in the range of 0.59–0.83×10⁻³ S·cm⁻¹, depending on the iodine content; that is, the greater the iodine content, the larger the conductivity of the complex.

The solid form of I₂-PVP was employed as an antimicrobial agent in cyanoacrylate compositions in a 10% to 20% by weight [189]. The antimicrobial activity of an n-butyl cyanoacrylate-based composition was more efficient against *Staphylococcus aureus*, and *Staphylococcus epidermidis*, and less against *Candida albicans*.

With the purpose of making an iodine-release composite for medical uses, Ahmad et al. [190] compounded gum acacia (GA), PVA, and I₂-PVP complex. Properties of the obtained material such as water resistance (swelling), thermal and mechanical properties were improved by crosslinking with glutaraldehyde. An intermolecular interaction between I₂-PVP complex and the hydroxy polymers occurred and positively affected these properties. In another report, Mazumdar et al. [191] devised tablets composed mainly of GA, EC, PVA, and the I₂-PVP complex, for water treatment. The tablet formulation showed significant bactericidal activity against four representative bacterial strains: *Escherichia coli*, *S. aureus*, *Listeria monocytogenes* Scott A, and *Salmonella typhimurium*.

### 2.2.2.2 Iodine-nylon complexes

Polyamides or nyons are important engineering materials, due to the unique combination of stiffness, toughness, lubricity, and resistance to abrasion, fatigue, and temperature that make them among the most versatile thermoplastics. They are featured by the intrinsic intermolecular hydrogen bonding in their chemical structures, which gives them a high tensile strength. Adversely, this hydrogen bonding has been thought to hinder the achievement of fibers with high mechanical properties (high modulus) when made by ultradrawing of high molecular weight polyamides [192]. To suppress the existing hydrogen bonding, an amount of energy <80,000 kJ/mol is required. Thus, to alleviate this drawback, the breakdown of the hydrogen bonds either by complexation with a Lewis acid such as GaCl₃ [193–195] or with iodine, has been viewed as alternatives to ensure the drawing processability. Since 1958, investigation on the structure changes of polyamides, mostly nylon-4, nylon-6, and nylon-6.6, upon iodination treatment, has been largely undertaken [196–202]. The results of such treatment were that the hydrogen bonds in both crystalline and amorphous regions were disrupted, and there was considerable chain mobility in the I₂-polyamide complex.
As early as 1966, Matsubara and Magill [203] studied the effect of sorption and desorption of iodine on the structures of 33 polyamides (even-even Nylons-x.y: 2.10, 6.6, 6.8, 6.10, 8.6, 8.8, 10.6 and 10.10; even-odd Nylons-x.y: 5.6, 7.6, 7.8, 7.10, and 9.6; odd-odd Nylons-x.y: 5.7, 7.7, 9.7 and 9.9; Nylon-x: 4, 6, 7, 8, 9, 10, 11, and 12). For sorption work, polyamides were treated with I2/KI aqueous solutions for a time extended from 15 min to 200 h. For some polyamides, the iodinating reagent was also employed in organic media such as methanol, chloroform, cyclohexane, and acetonitrile. The different complexes were thought to involve not I2 molecules, but I3- species, as evidenced by its characteristic IR band at 140 cm-1 and by the similarity between the spectra of iodine-treated polyamides and of the N-acetylacetamide-I3- complex. The iodine sorption extent was a function of the polyamide chain length; it decreased with an increasing number of methylene groups. Before iodine treatment and after iodine removal (with sodium thiosulfate), the two types of amides shown in the IR spectra appeared at around 690 cm-1 and 580 cm-1 for nylons with an α structure, and 715 cm-1 and 630 cm-1 for those with a γ structure. Treatment with I2/KI altered these absorptions and brought up structure changes (α to γ or γ to α).

Tonelli et al. [204], in their project, mentioned the complexation of iodine with nylon-6.6 using I2/KI solution. From IR spectral analysis, I2-nylon-6.6 was distinctive by an absorption band appearing at 3390 cm-1, assigned to the non-bonded NH (that of bonded NH appeared at 3300 cm-1), suggesting hydrogen bonding destruction as traced in Scheme 3. The iodinated nylon was easily processed from the melt and finally treated with sodium dithionite to restore the destroyed hydrogen bonds. Such iodine-inducing hydrogen bond breaking in nylon-6.6 has been discussed [205].

As with the above polymers, the species found in the I2-nylon complexes such as I2-nylon-6 were the polyiodide ions I5- and I3- as spectral analyses (13C NMR, 14N NMR, IR, Raman, XRD) suggested [199, 200]. In the I2-nylon-6 complex prepared by treating nylon-6 with I2/KI solution, the I5- ions were normal to the chain axis and the I3- units were oriented along the polymer chain. Murthy et al. [200] ascertained that the three reflections at 15.6, 4.55, and 3.0 Å observed in the XRD spectra of iodinated oriented nylon-6 film, were associated with iodine in the nylon matrix; the first one was due to a complex between nylon and I3- and the last two reflections to I5- ions columns. Raman spectra of the I2-nylon-6 complex revealed peaks at 113 cm-1 and 169 cm-1, assigned to I3- and I5-, respectively [199]. In another report, Murthy [198] proposed that, based on the small-angle X-ray scattering (SAXS) data, the iodide ions in freshly iodinated nylon-6 were more concentrated in the crystalline regions of the polymer than in the amorphous one. The I5- ions columns, believed to be in form of H+ I5-, were thought to interact strongly with nylon-6 chains, whereas the I3- ions, believed to be in form of K+ I3-, were weakly bound to the chains. The species I5- was thought to exist in the lamellar crystalline of the polymer and was easily desorbed, whereas the I3- species existed in two forms: a less stable form with an I-I distance of 3.2 Å, and a more stable form with an I-I distance of 3.08 Å. The lattice formed between I5- ions columns and nylon-6 chains, twisted the amide group out of the polymer matrix plane (Figure 11), which gave rise to hydrogen bonds between parallel chains upon iodine desorption. 13C NMR analysis showed that the carbonyl peak in the complex is downfield from that for the analogous carbons in the α, γ, and amorphous nylon-6 structures; chemical shifts of the carbonyl of α and γ crystal states...
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weight of iodine) and demonstrated that the involved I$_5^-$ ions could be converted to I$_3^-$ ions upon aging, while complexed with nylon-6. Thermal analysis revealed that the latter ions could be transformed into the former ones at around 75°C, a result of “melting” and “recrystallization” of the iodide ion arrays, as illustrated in Scheme 4.

By contrast, the coordination between polyiodides I$_n^-$ and nylon-6 occurred rapidly and drastically within polyiodide solutions, and the responsiveness in the complex with other molecules was enhanced by coordination [207], rendering the incorporation of novel functionality with other molecules, ions or salts into the polyamide matrix, more readily.

Barnes [201] patented his invention on the complexation of nylon-4, also known as polypyrrolidone, with iodine and its biological activities. The complex could be formed either by exposure to iodine vapor, mixing with iodine crystals, or dipping in I$_2$/KI solution. In another work [202], this complex was prepared by adding aqueous I$_2$/KI solution to an aqueous dispersion of a wet cake of I$_2$-nylon-4, previously made by precipitating nylon-4 from its solution in its monomer (2-pyrrolidone) into water. I$_2$-nylon-4, with higher iodine content, was dark chocolate-brown when wet and became black in a dry state. A maximum uptake of 20% of iodine by nylon-4 was estimated, and beyond that extent, a degradation of the polymer occurred. Desorption of iodine from the complex in boiling water or in an oven at 100°C can be completed in a few minutes, giving back the colorless nylon-4. The complex exhibited bactericidal and fungicidal properties against *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Proteus mirabilis*, and *S. aureus*. Singhal et al. [208] also reported good antibacterial activity of iodine-doped nylon fibers towards the same biological strains, and found that this antibacterial activity decreased with the release of iodine in water; the release of iodine in distilled water was sustained for about 30 days. The I$_3^-$ ions were believed to be responsible for the observed antibacterial activity.

As to the influence of the method on the behavior of I$_2$-nylon, Singhal and Ray [209] investigated the iodine

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![Figure 11](image_url)  
*Figure 11* Proposed lattice match between I$_5^-$ columns and nylon-6 chains along the fiber axis. Reprinted with permission from Ref. [206]. Copyright (1993) American Chemical Society.

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![Scheme 4](image_url)  
adsorption onto I₂-nylon-6 prepared by immersion and exposure methods. The iodine adsorption from dipping the nylon in acetone was not Langmuir-type, but that from exposure to iodine vapor showed a pseudo-Langmuir behavior. The same isotherm Langmuir absorption was advanced for I₂-nylon-6, prepared by immersion of nylon-6 into aqueous solution of I₂/KI at 25°C, by Sukawa et al. [210].

Kang and Lee [211], Jeong et al. [212] and Shin et al. [213] studied the behavior of iodinated nylon-6 before (IBF) and after film forming (IAF). The iodine uptake by nylon-6 in forms of powder and film increased with I₂/KI concentration up to 0.6 N, that of the powder form being the greater, as it possesses the greater specific surface area [211]. Beyond this concentration, the adsorption extent leveled off for both forms. The investigation on the weight loss of the two types, IBF and IAF, by TGA measurements, indicated a different content of iodine on the polymer due to the iodine evaporation during the melt-press processing. DSC analyses revealed that the melting point of IAF was shifted from 220°C of the untreated nylon-6 to a lower temperature, and the endothermic peak became broader and smaller, then practically disappeared at 1.0 N, with an increasing concentration of I₂/KI. FTIR spectroscopy suggested that the crystallinity extent decreased or disappeared upon treatment with I₂/KI concentration. However, DSC curves of IBF films indicated that they were practically amorphous, as shown by a small endothermic peak at 155°C. The FTIR bands of IBFs at 1464 cm⁻¹, 1439 cm⁻¹, and 980 cm⁻¹ of the amorphous structure, increased gradually with increasing concentration of I₂/KI, and those at 1478 cm⁻¹, 1418 cm⁻¹, 1200 cm⁻¹, 1028 cm⁻¹, 961 cm⁻¹, and 930 cm⁻¹ of the crystalline structure decreased, but did not disappear. This investigation was in tune with the fact that the I⁻ ions were normal to the chain axis and the I⁻ units were oriented along the polymer chain as observed by Murthy et al. [197, 200].

Elsewhere [212], a thorough work on the effect of temperature and time of the preparation of IBF films on their thermal behavior was undertaken. The results provided the film containing less I₂/KI and treated at higher temperatures exhibited peaks that are associated with the more stable type of crystal among the complex crystal, the relaxed γ- and α-crystals. These peaks increased with increasing the temperature and prolonging the time. The findings of their TGA measurements were that the weight loss curve had two distinguishable weight loss zones: a lower-temperature zone associated with volatilization of I₂ molecules isolated from I⁻⁻ ions, and a higher-temperature zone associated with decomposition of I⁻⁻ ions and nylon-6 molecules. An oxidizing action of the I₂ molecules generated in the course of the TGA measurement was noticed, thus reducing the degradation temperature of the nylon-6 chains. Later, Shin et al. [213] reported the effect of deiodination of IBF by dipping in water/ethylene glycol (EG) solutions of sodium thiosulfate. After deiodination, the sorption degree of the films and the time necessary for complete deiodination were found to increase and to decrease, respectively, with increasing temperature and EG content. Also, the deiodination provoked crystallization of the amorphous IBF film. Indeed, in the presence of EG in the deionizing system, α-crystal was obtained at temperatures >55°C. However, at a lower temperature, both α- and γ-crystals were formed with melting points at -220 and -215°C, respectively.

Yamamoto et al. [162, 196, 214, 215] and Hishinuma and Yamamoto [216] embarked on the investigation of the electrical conductivity σ of iodinated nylon-6 adducts and their composites, to evaluate them as positive electrodes. The Iₐ-nylon-6 complex was prepared by mixing powdery nylon-6 with molecular iodine at temperatures of 115°C and 145°C, giving black solid with iodine content of 82 wt%, and viscous liquid with iodine content of 87 wt%, respectively. The conductivity of both complexes was found to increase with iodine content and reached maximum values at σ≈ 10⁻³ S·cm⁻¹, values comparable with those of iodinated π-conjugated polymers [214]. Through XRD and IR analyses, the authors confirmed the destruction of crystallinity of the virgin nylon-6 upon iodination. They extended their work on the electrical conductivity to Iₐ-nylon-6/carbon powder composite; the conductivity was found to rise with carbon powder content, and reached better values (σ≈10⁻¹ S·cm⁻¹) even at an iodine content ≤50 wt%, presumably due to the formation of carbon network in the nylon-6-carbon powder mixture.

In another paper, Yamamoto and Kuroda [198] evaluated Iₐ-nylon-6 adducts, prepared by dipping a nylon film into an organic solution of iodine and by exposing the film to iodine vapor, as positive electrodes of galvanic cells. When acetone was experimented on as an organic medium, nylon film was found to absorb iodine smoothly and became brown; the iodine uptake by the nylon increased with increasing iodine concentration up to 0.10 mol·l⁻¹. The equivalent absorption extent was observed with moderately polar solvents, such as CHCl₃ and THF, but the absorption amount of iodine was less when more or less polar solvents were experimented. An electrical conductivity σ of 4×10⁻⁴ S·cm⁻¹, an electromotive force (e.m.f.) of 1.42 V, and an electric current I of galvanic cell of 2.6 mA·cm⁻² were measured for the thus-prepared adduct. With the Iₐ-nylon-6 sample from vapor process, about similar e.m.f. (1.44 V) and I (3.1 mA·cm⁻²) values were obtained. In this work, other Iₐ-polymer
adducts [polymer: PVA, PVP, P2VP, poly(2,5-thienylene) s, poly(phenylene sulfide), poly(acrylamide), poly(N-vinylcarbazole)] were prepared and evaluated as positive electrodes of galvanic cells.

A sound investigation on the effect of iodine treatment on the FTIR spectral changes of nylon-6 and desorbed nylon-6 was undertaken by Maillo et al. [217]. The treatment of a thoroughly prepared nylon-6 with different concentrations of aqueous I2/KI solutions revealed significant changes in the absorption bands of the different kinds of amide group, resulting in a hydrogen bond breaking; a number of absorption bands were shifted either downward or upward with increasing or decreasing intensities. Water molecules were thought to facilitate the complex formation, promoting the hydrogen bridges breaking. Also, the crystallinity of nylon-6 dropped when treated with iodine, as suggested by the intensity decreasing of the conspicuous band at 1260 cm\(^{-1}\), a band associated with crystallinity of the material. Spectra indicated that the complex is formed between the I\(_{3}^-\) ion and the CO and NH groups of the nylon, which confirmed the results advanced by an early work [203].

The FTIR spectrum of the desorbed nylon-6, resulting from treatment of I\(_{2}\)-nylon-6 with sodium thiosulfate, suggested that the pristine nylon-6 underwent a crystallization transition from \(\alpha\) to \(\gamma\) form.

Kawaguchi [218–221] and Kawaguchi and Tsuratani [222] endeavored to decipher the structure changes of the I\(_{2}\)-nylon-6 complex. Intercalated structures composed of iodine, in which polyiodide ions were coordinated between hydrogen-bonded sheets of nylon-6 were seen. The spacing of the sheets was 1.95 nm in the irregular intercalation, while it is 1.56 nm in the ordinary specimens, which was considered to be due to the intercalation of iodine layers between every hydrogen-bonded sheet of nylon-6. Kawaguchi [223–225] extended his efforts to elucidate the effects of moisture and cation addition on the conductivity of I\(_{2}\)-nylon-6 complex. This material, when aged in normal atmosphere, showed a positive dependence of conductivity on temperature under applying sequential direct current (dc) field. The rapid and positive response of conductivity to the dc field indicated an ionic conduction in the swollen complex, and the slow change was attributed to moisture. However, when aged in vacuo at room temperature for more than 2 weeks after doping, a little change of conductivity was noted. Also, the conductivity was found to vary with humidity (relative humidity, RH) and with the mobility of cation added [226]. From mass considerations, it was thought that the polyiodides (I\(_{3}^-\)) and the added cations adsorbed not only in the amorphous phase, but also in the crystal phase of the complex and could be released when the complex became swollen; the polyiodides, which quickly diffused into the crystal phase, were gradually liberated through the swollen amorphous phase in the high RH environment.

Optical properties, such as refractive index and birefringence of drawn nylon-6, were improved upon iodination with iodine vapors, as a result of structure changes [227]; the iodination with iodine vapors was conducted at different periods of time from 30 to 120 min. The refractive indices and the birefringence values were proportional to the time of iodine evaporation. Moreover, the iodine treatment increased the isotropic refractive index, the mean polarizability per unit volume, the surface reflectivity, and the orientation function.

Sukawa et al. [210] reported that the sorption isotherm of molecular iodine by nylon-6 was in accordance with the Langmuir model, as were those of PVA, poly(acrylamide), poly(4-vinylpyridine), poly(tetramethylene ether glycol), poly(acrylonitrile), and poly(3-vinyl-10-methylphenothiazine).

Refat et al. [228] investigated the complexation between molecular iodine and poly(amidoamine)-containing dendrimers (D1 and D2) (Figure 12). A chloroform saturated solution of iodine was mixed to a chloroform saturated solution of each of the dendrimers for 15 min at room temperature under stirring. The formed complexes I\(_{2}\)-D1 and I\(_{2}\)-D2 were brown and the iodine contents were, respectively, 13.55% and 6.28%. Their electronic absorption spectra showed two bands at 269–282 nm and 435–438 nm. The stoichiometry for the CT formation was 1:1 for I\(_{2}\)-D1 and 2:1 for I\(_{2}\)-D2 (2 I\(_{2}\) for 1 D2).

These stoichiometries were supported by IR and thermal analyses. The thermal stability for the I\(_{2}\)-D2 complex was greater than that for the I\(_{2}\)-D1 complex, a behavior that can be explained on the basis of the stability of D2 and the number of attached donor sites.

2.2.2.3 Iodine-polyaniline complex

Being a polyamine, aniline polymers are prone to react with molecular iodine by CTC to form I\(_{2}\)-doped polyaniline (PANI). Luo and his co-workers [229] prepared this complex with an amount of iodine of 37 wt\%, by mixing polyaniline base with iodine in acetone for 4 h at ambient temperature. The infrared analysis indicated that the main bands of I\(_{2}\)-PANI were shifted to lower wavenumbers, resulting from iodine binding; the absorption bands at 1164 cm\(^{-1}\) and 1579 cm\(^{-1}\) were displaced to 1564 cm\(^{-1}\) and 1095 cm\(^{-1}\). The thermal stability of the complex was lower than that of the pristine PANI; drastic decomposition of the complex started nearly at 270°C and that of the untreated
PANi commenced at about 340°C. Also, X-ray diffraction analysis proved that the iodine binding did not alter substantially the amorphous morphology of PANi.

Morales et al. [230] prepared PANi by plasma polymerization of aniline in the presence of iodine vapor, using a radio frequency (rf) glow discharge at 13.5 MHz and an average power of 18 W. The polymerization was run at 92°C for different times (60–240 min) and in vacuo (1.5×10⁻³ mBar). Such I₂-PANi complex in form of thin film underwent morphological changes during heating-cooling cycles (152 to 22°C). This phenomenon resulted in an increasing of its electrical conductivity (σ); an extent of crystallinity was created upon such cycles. The variations of σ with the reverse of temperature either on heating or on cooling followed Arrhenius behavior, with activation energies $E_a$ between 0.1 to 1.2 eV, suggesting semi-conducting materials. At about 110°C, $\sigma$ for iodinated polyaniline was almost 1×10⁻⁹ S·cm⁻¹.

Gizdavic-Nikolaidis and Bowmaker [231] doped the emeraldine base form of polyaniline (EB-PANI) with molecular iodine vapor under reduced pressure (10⁻³ Torr) for two days and at a temperature of 20°C. The doping level of iodine in the I₂-EB-PANI was gravimetrically found to be 8.2%. The FTIR spectrum of the thus-doped PANi revealed shifts of 1586 and 1158 cm⁻¹; a new band at 133 cm⁻¹ appeared in the far-IR spectrum, which was assigned to the $\nu_3$ mode of $I_3^-$. Thus, these observations strongly indicated that the iodination took place on the quinoid units in the polyaniline molecular chains while the benzoid units remained essentially unaffected. Interestingly, the presence of iodine in the polymer enhanced the EPR signal by almost five-fold. This ESR signal enhancement was also observed by Goto [232] when doping a composite made of EB-PANI and pulp paper with iodine vapor. Based on FT-IR, electron paramagnetic resonance (EPR), and $^{13}$C NMR analyses, the structure of I₂-EB-PANI was proposed as shown in Figure 13. The conductivity of the EB-PANI was increased by five orders of magnitude through the iodine-doping process, reaching a value of $\sigma=0.504$ S·cm⁻¹.

Stejskal and his co-workers [233] iodinated EB-PANI with molecular iodine in a water-ethanol medium for 1

![Figure 12](image_url) Poly(amidoamine)-containing dendrimers. Reprinted with permission from the corresponding author of Ref. [228].

![Figure 13](image_url) I₂-EB-PANI complex.
week at room temperature. As with Gizdavic-Nikolaidis and Bowmaker’s work [231], the electrical conductivity increased by five orders of magnitude, a result that was thought to stem from the protonation of PANi with the hydriodic acid that was produced in the oxidation of EB-PANi by I₂ to the pernigraniline form. The conductivity jumped from 10⁻⁹ S·cm⁻¹ for EB-PANi to 7×10⁻⁴ S·cm⁻¹ for PANI doped at a molar ratio [I₂]/[PANI]=3.

About a decade earlier, Zeng and Ko [234] reported the electrical conductivity of iodine-doped PANi to be 1.83×10⁻³ S·cm⁻¹, almost eight orders of magnitude greater than that of the virgin PANi (4.26×10⁻¹⁰ S·cm⁻³); the I₂-EB-PANi was realized by stirring a mixture of the polymer with an ethanolic solution of molecular iodine for 48 h at room temperature. Their results confirmed that the iodination reaction occurred mostly on the nitrogen atoms of the quinoid units as illustrated by other workers [231, 233]. In addition, the polyiodide ions were mostly I⁻₃ and I⁻₅, the latter being predominant at a higher doping level. In this research, the doping level of iodine in the I₂-EB-PANi was determined to be only 6 wt%, that is, less than that reported by Gizdavic-Nikolaidis and Bowmaker [231]. By iodine doping, the amorphous state of PANi was reduced towards regularity, as revealed by WAXD analysis. Both thermal stability and moisture uptake of PANi decreased upon iodination.

Furthermore, Aya et al. [235] proved that iodination solution effected, besides doping, the ring iodination of EB-PANI films, and mainly its oxidation to a pernigraniline state. A sensor of iodine in aqueous solutions based on EB-PANI-coated electrode of the QCM (quartz-crystal microbalance) was developed.

The iodine-doping of alternating current (ac) plasma polymerized aniline thin films was also reported by Mathai et al. [236] and Sajeev et al. [237]. Iodination techniques included the iodine chamber method (iodine crystals were placed in a glass beaker and the films to be doped were kept above this glass beaker) and in situ iodine doping (both monomer and the dopant iodine were sprayed simultaneously into the plasma zone). The optical bandgap of iodine-doped samples was reduced to 1.80 (iodine chamber method) and 2.42 eV (in situ iodine doping) when compared with that of pure polyaniline (3.04 eV). This bandgap increased to 3.01 and 2.61 eV, respectively, when the doped PANI samples were heated at 100°C for 5 h, probably due to the removal of iodine atoms that were adsorbed on the surface or loosely bonded to the polymer. The in situ iodine doping technique seemed to be more reliable. However, the reduction in the optical bandgap was more pronounced in the case of rf plasma polymerized aniline films, a result that was attributed to the conjugation arising out of the increased power during rf plasma polymerization.

It is worth citing the catalytic capacity of I₂-EB-PANI, among other PANi dopants, in the synthesis of 3,3’-bis(indolyl)phenylmethane with quantitative yields (99% for a reaction time of 4 h and at room temperature) from indole and benzaldehyde [238].

Aniline and dimethylaniline were polymerized via oxidative dehydropolycondensation in the presence of iodine at a temperature range of 120–300°C for a time of 10 h [239]. At 175°C and a time of 2 h, increasing iodine afforded a decrease in the yield of the polyaniline and an increase in the yield of aniliniodohydrate, a competing product. The polyaniline (aniline black) was found to contain 52–62% of iodine at any polymerization temperature, to be readily soluble in DMF and partially soluble in chloroform, and to be highly stable in air over a period of a year. A concomitant formation of I₂-PANi occurred. The polyaniline obtained showed a high electrical conductivity, 3.8×10⁻³ S·cm⁻¹ (for 56% iodine content) against 10⁻¹⁰ S·cm⁻¹ for polyaniline. An infrared spectrum put forward the existence of bands attributable to the -NH⁺ group (2960 cm⁻¹), the -NH₂⁺ group (2588 cm⁻¹), and the -NH group of iodohydrates (1620 cm⁻¹). UV analysis demonstrated the existence of I⁻₃ (295 nm), and long polyiodiated chains (I⁻₅) (520 nm, 550 nm, 600 nm, 655 nm). Alkali treatment of the polymer led to an increase of I⁻₃ content and a decrease of polyiodiated chains.

2.2.2.4 Iodine-polypyrrole complexes

Morales et al. [230] also polymerized pyrrole (py) under the above-mentioned plasma conditions, affording I₆-Ppy. Only with polymers prepared at 240 and 300 min, the σ=f(1/T) showed linear Arrhenius behavior, with $E_a=1.1$ eV. At about 110°C, $\sigma_{\text{room}}$ of iodinated polypyrrole was almost 1×10⁻⁶ S·cm⁻¹. The heating-cooling cycles did not appreciably alter the inner structure of the polymer, and showed an amorphous region with a small crystalline region. The same research group [240] tackled the plasma copolymerization of aniline and pyrrole in the presence of molecular iodine at different reaction times. It was found that the conductivity of aniline-pyrrole copolymers prepared in the absence of iodine varied between 10⁻¹² and 10⁻⁹ S·cm⁻¹, and varied linearly with the relative humidity (RH). However, the I₁-copolymers had their conductivities in the range of 10⁻⁹–10⁻⁸ S·cm⁻¹, and a drastic rise in conductivity was seen at RHs higher than 80%. No clear impact of the aniline/pyrrole molar ratio on the conductivity was detected. In another report, Morales and his team [241] fabricated iodine-doped thin films in the form...
of bilayer polymers of aniline and pyrrole, by plasma polymerization under identical above-cited conditions. The electrical conductivity of such thin films ranged from $3.7 \times 10^{-9}$ to $2 \times 10^{-8}$ S·cm$^{-1}$; conductivities of polyaniline and polypyrrole were lower than that of the bilayer composite, $2.6 \times 10^{-11}$ and $8 \times 10^{-11}$ S·cm$^{-1}$, respectively.

Kumar et al. [242] polymerized pyrrole by means of the plasma method ($f_{RF} \sim 13.56$ MHz) in the absence and in the presence of iodine. Based on IR analyses, the iodine was neither bonded in any way, nor strongly interacting with the pyrrole polymer chains. The structure of Ppy made by the plasma technique was therefore proposed as shown in Figure 14. Yet, the presence of iodine made the surface morphology of the Ppy film smoother, and brought about an increase in the connectivity and continuity between the blocks of polymer chains. Electronic spectra showed bandgap energies of 1.3 and 0.8 eV for the undoped and doped Ppy films, respectively. The conductivity of the doped Ppy film was approximately twice that of the undoped one.

### 2.2.2.5 Iodine-polypyridine/poly(N-vinylcarbazole)/poly(N-vinylimidazole) complexes

$N$-Heteroaromatic-bearing polymers were able to bind molecular iodine to form $n \rightarrow \sigma$ iodine-polymer complexes. Pyridinic polymers can bind chlorine, bromine, and iodine molecules, by a CTC mechanism via the nitrogen atom of the pyridine unit. Polymer-supported bromine/chlorine complexes were found to be efficient halogenating and oxidizing agents of organic molecules [243–246]. Lithium primary cells based on iodine-poly(vinyl pyridine) with a shelf-life of 10 years were reported [247].

Arzumanyan and his collaborators [248] polymerized pyridine to polypyridine in the presence of excess iodine, at a temperature range of 160–240 °C for 0.5 h to 5 h. The actual polypyridine with a molecular weight of about 2000 was an iodine-polymer complex and was a black powder, soluble in DMSO, THF and DMF. The complex was paramagnetic and the actual iodine species were $I^-$ and $I_3^-$ according to X-ray electron spectra, depending on the initial iodine concentration. Also, such analysis also hinted at two types of nitrogen in the polypyridine complex; pyridine nitrogen ($E = 399.8$ eV) and quaternary ammonium nitrogen ($E = 402.4$ eV).

Russian chemists [249] reported the synthesis of poly($N$-methyl-4-vinyl pyridinium triiodide) (Figure 15) by reacting P4VP with methyl iodide, to give poly($N$-methyl-4-vinyl pyridinium iodide), followed by reaction with molecular iodine in a water-alcoholic solution. The complex was a dark brown powder with a $T_g$ of 180 °C and a $T_m$ of 243–245 °C. The UV-visible spectrum of the complex showed three absorption bands at 295 nm, 367 nm, and 460 nm. This iodine complex was tested for its biological activity and it was found that its minimum inhibition concentration (MIC) against *Vibrio cholerae* was 1 mg·ml$^{-1}$, compared with 0.25 mg·ml$^{-1}$ against *E. coli* and *S. aureus*. However, the bactericidal activity of poly($N$-methyl-4-vinyl pyridinium iodide) manifested at a MIC of 5.6 mg·ml$^{-1}$.

$p$-Toluenesulfonic acid (PTSA) was found to be able to stabilize the electrical conductivity of $I_2$-P4VP [250]. The highest conductivity, approximately $10^{-3}$ S·cm$^{-1}$, was obtained for [iodine]/[monomer unit] molar ratio of 1.5, compared to $10^{-14}$ S·cm$^{-1}$ for P4VP at room temperature. The conductivity of the complex decreased at high temperatures by three to four orders of magnitude, due to the large diffusion of molecular iodine. PTSA was thought to reabsorb the iodine molecules and restored such conductivity.

![Figure 14](image1.png) Figure 14 Proposed structure for Ppy; $X=(A)$, (B), (C), (D), (E), (F). Reprinted with permission from Ref. [242]. Copyright (2003) American Institute of Physics.

![Figure 15](image2.png) Figure 15 Poly($N$-methyl-4-vinyl pyridinium triiodide).
Chetri et al. [251] iodinated a nano P2VP made by electrolysis of a hydrochloric complex (P2VP·HCl), in view to making a lithium-iodine battery. The procedure was to allow the sublimed iodine to be in contact with the nano P2VP thin film (0.2 μm) for 16 h at 25°C. A color change was observed from a brown color (pristine film) to a violet one (iodinated film). A characteristic IR band due to the presence of iodine in P2VP was seen at 1550 cm⁻¹, which was absent in the nano P2VP. UV analysis showed a blue shift from 194.4 (nano P2VP) to 191.5 nm (nano I₂-P2VP).

The electrical conductivities of the polymer and its iodinated form increased with temperature and were stable up to 150°C. In this research, the conductivity of the nano I₂-P2VP was unexpectedly less than that of the normal I₂-P2VP. Owing to its nano fine structure, the former material was more thermally stable than the latter one; up to 200°C, a weight loss of only 10% was measured for the former, whereas about 50% of a weight loss was detected for the latter one.

Jandrey et al. [252] checked the influence of the structure of the poly(2-vinylpyridine-co-styrene-co-divinylbenzene) on the iodine capacity and the antibacterial activity of the complex. The complex was made either by mixing the copolymer beads with grinded iodine at 27°C for 72 h, or by adding 1,2-dichloroethane to the mixture, and the system was kept under identical conditions (Scheme 5). The first method afforded a higher loading capacity than the second one, 83% against 71% for the 2VP/St/DVB=70/20/10 copolymer; the lower DVB content is within the copolymer, i.e., the lower the crosslinking, the higher the loading. The different complexes from both methods were dark brown beads. All iodine-copolymer complexes presented significant antibacterial activity against E. coli. Indeed, for initial bacteria concentration ranging from 3.8×10³ to 3.3×10⁷ cells·ml⁻¹, the activity of the complexes synthesized by the first method was 100% in most cases, and was 100% for the 70/20/10 copolymer complex synthesized by the second method for 2.2×10⁶ cells·ml⁻¹.

Aronson et al. [253] studied the electrochemical and conductivity properties of the iodine complexes of cyclized poly(acrylonitrile) (CPAN) (Figure 16A) and poly(2-vinylpyridine) (P2VP); the complexes were formed by exposing the polymers to iodine vapor. The e.m.f. values for I₂-P2VP samples annealed at 50°C, 70°C and 90°C approached that of pure iodine at a molar ratio of about 2.3. Electrical conductivity for I₂-CPAN and I₂-P2VP samples at room temperature, as a function of iodine uptake, reached plateaus (~10⁻³ S·cm⁻¹) at mole ratios of about 1.0 and 2.3, respectively. E.m.f. methods gave the free energies (ΔG) of formation of iodine complexes and were -2 and -3.2 Kcal/mol of I₂, respectively. The nature of these two complexes seemed to be considerably different from I₂-polycetylene; that is, CPAN and P2VP were able to absorb significantly more iodine and attained electrical conductivities several orders of magnitude lower than polycetylene and, unlike polycetylene, the complexes were stable in air for long periods of time. Also, the electrical conduction mechanism in these two complexes may be much different from that in I₂-polycetylene. Tayyan and his co-workers [254] treated poly(N-vinylcarbazole) films (Figure 16B) with a molecular weight of 1,100,000 with iodine by immersion in a chloroform solution at room temperature. The dc conduction of the doped polymer followed the Schottky mechanism, and the thermal activation energy of the dc conduction was ~0.47 eV.

Films of poly(N-vinylimidazole) (PVI) with a molecular weight Mₘ of 200,000 and quaternized with methyl iodide (Figure 16C) were exposed to iodine vapor under nitrogen atmosphere [255]. The glass transition temperatures of PVI, quaternized poly(N-vinylimidazole) (QPVI), iodine-doped PVI, were 373 K, 354 K, and 375 K, respectively; iodine-doped QPVI was flexible at room temperature. The iodine-doped PVI and iodine-doped QPVI were insoluble, due to the formation of ionic crosslinks within the polymers.
polymer network. The maximum conductivity achieved was $10^{-7}$ S·cm$^{-1}$ for the first complex, with a molar ratio of $[\text{I}_2]/[\text{(vinylimidazole unit, VI)}]$ of 0.6 and $10^{-4}$ S·cm$^{-1}$ for the second one, with a $[\text{I}_2]/[\text{VI}]$ molar ratio of 2.0. While the conductivity of the second complex did not change appreciably after 22 days of exposure at ambient atmosphere, that of the first complex dropped to a value $10^{-10}$ S·cm$^{-1}$.

The temperature dependence of ionic conductivity of these two systems fitted the Arrhenius equation.

In another work, PVI, with a molecular weight $M_w$ of 107,000, was allowed to react with iodine in the presence of HNO$_3$ to yield an iodinated PVI (Scheme 6) [256]. The latter product containing about 20.4 wt% of iodine as covalent C–I, was tough, transparent, yellow brown, and insoluble in methanol. The conductivity of iodinated PVI was measured as $10^{-5}$ S·cm$^{-1}$ and lasted for months under aerobic conditions. It was reasoned that this constant conductivity was an indication of a more stable CTC formed by ionization, leading to a positively charged polymer with I$^-$ as a counterion. The thermal transition $T_g$ increased from 109°C of the pristine polymer to 132°C after iodination. Such increase in $T_g$ was rationalized in terms of restriction of segmental motion, due to the large iodine atoms in the repeating units, and to I$^+$ bridges acting as crosslinking centers. This iodinated PVI behaved differently from the iodine-doped PVI. Indeed, the conductivity of the latter material was not retained in atmospheric conditions, and decreased within a few days (from $10^{-7}$ to $10^{-10}$ S·cm$^{-1}$) and the $T_g$ was not affected by iodine doping.

### 2.2.2.6 Iodine-poly(Schiff base)s complexes

Polyazomethines or polyimines, commonly known as poly(Schiff base)s, have the propensity to develop complexes with molecular iodine, mainly to improve the electrical property of the conducting polymers. Poly(Schiff base sulfide)s (PSBS) (Figure 17) were prepared in 95% from their monomers and sodium sulfide as orange-brown colored materials with intrinsic viscosities of 0.18–0.68 dl·g$^{-1}$ [257, 258]. PSBSs were then immersed into a saturated chloroform solution of iodine, to make iodine-doped polymers; a slight color change was noticed for all polymers. The conductivities of I$_2$-PSBS complexes were in the range of $5.5 \times 10^{-4}$ to $2.1 \times 10^{-3}$ S·cm$^{-1}$, and were greater when compared with those of the undoped polymers, $4.4 \times 10^{-12}$ to $9.9 \times 10^{-11}$ S·cm$^{-1}$. In general, the conductivity of the doped polymer increased linearly with doping extent up to a certain value and leveled off beyond. The doped structure of the last PSBS is shown in Figure 18, giving an insight into the type of complexation and showing that the sulfur atom was not the electron donating site. Batteries with iodine-doped PSBS as the cathode and lithium as the anode were made with an open-circuit voltage of 3.3 V, a short-cut circuit current of 2.2 A, and an energy density of 268 W·h·kg$^{-1}$.

**Scheme 6**  Iodine treatment of poly(N-vinylimidazole).

**Figure 17**  Some poly(Schiff base sulfide)s (PSBS).

**Figure 18**  Iodine-doped poly(Schiff base sulfide)s (PSBS).
The same research team [259] studied the electrical properties of the iodine-doped poly(Schiff base)s pictured in Figure 19A. These poly(Schiff base)s were obtained by polycondensation of \( p \)-phenyldiamine and a glyoxal derivative at a temperature range of 25–165°C, and in the presence of ZnCl₂ as catalyst. The polymers were brown with intrinsic viscosity ranging from 0.10 to 0.18 dl·g⁻¹ and were soluble in some organic solvents such as diethyl ether, benzene, xylene, cyclohexane, and carbon disulfide. The polymers turned black upon doping with iodine. The conductivities of iodine-doped poly(Schiff base)s ranged from \( 4.1 \times 10^{-4} \) to \( 1.5 \times 10^{-3} \) S·cm⁻¹, whereas those of the original polymers ranged from \( 6.11 \times 10^{-12} \) to \( 2.90 \times 10^{-11} \) S·cm⁻¹.

Li and Wan [260] synthesized poly(Schiff base)s, PPpP and PPmP (Figures 19B and C), by polycondensation of 2,6-pyridine dicarboxaldehyde with \( p \)-phenylene diamine and with \( p \)-phenylene diamine. Complexation of these polymers with molecular iodine was performed by grinding the mixture of the polymer with iodine into a fine powder and then immersing the latter powder into absolute ethyl alcohol, followed by evaporation of this solvent. Both polymers were yellow solids, insoluble in common solvents, and infusible. Upon iodine treatment, the polymers turned brown to black, depending on the doping extent. IR and UV-visible spectra of PPpP and PPmP changed upon treatment with iodine, particularly at higher dopings. At low dopings, the charge transfer (CT) may have occurred between non-bonding electrons of the nitrogen atom of the poly(Schiff base) and iodine, and the polymer structures did not change. However, at high dopings, the CT could have occurred between the \( \pi \)-electrons in the poly(Schiff base) and the iodine, and the structures have changed. The conductivities of I₂-PPpP and I₂-PPmP increased by three to four orders of magnitude (\( 10^{-10} \) to \( 10^{-11} \) S·cm⁻¹ for the pristine polymers). The magnetic susceptibility of CTC I₂-PPmP was found to be dependent on the doping degree.

Hajduk et al. [261] doped films prepared from polyazomethine, 1,4-phenylenemethenetricrilonitrile-1,4-phenylenenitrilomethylene (PPI) (Figure 19D), with iodine vapor for several days (up to 12 days). The doping mechanism was believed to involve the removal of electron from PPI \( \pi \)-system by I₂ molecules and the formation of counterions I₃⁻. The formation of a positive polaron means that doping of polyazomethine PPI is of \( p \)-type.

Kaya and Bilici [262] polymerized oxidatively 4-[(pyridin-2-yl-imino)methyl]phenol (4-PIMP) using either NaOCl, H₂O₂ or O₂ in aqueous KOH, at 50–90°C and for a time of 3–15 h (Scheme 7). The polyazomethines, obtained in high yields (74–99%), were of low molecular weights (\( M_n=4450; \) MWD=1.169) when NaOCl was used as the oxidizing agent.

\[
\text{R} = \text{H, CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3
\]

**Figure 19** (A) Poly(Schiff base)s from polycondensation of \( p \)-phenyldiamine and a glyoxal derivative, (B), poly(Schiff base) (PPpP), (C), poly(Schiff base) (PPmP), (D), 1,4-phenylene-methenentricrilonitrile-1,4-phenylenenitrilomethylene (PPI).

\[
\text{NaClO/H}_2\text{O}_2 \text{ or air O}_2 \text{ Aq. KOH}
\]

**Scheme 7** Polymerization of 4-[(pyridin-2-yl-imino)methyl]phenol (4-PIMP).
They were dark brown powders, completely soluble in DMF, DMSO and aqueous alkaline or concentrated H₂SO₄ solutions, and insoluble in heptane, acetone, THF, hexane, benzene, toluene, acetonitrile, methanol, ethanol, CH₂Cl₂, CCl₄, and dioxane. The electrical conductivity of polyazomethines increased upon iodine-doping for 48–60 h, and was nearly $5.40 \times 10^{-7}$ S·cm⁻¹; that of the polymer was about $4.9 \times 10^{-8}$ S·cm⁻¹. The suggested coordination mechanism of iodine with poly(Schiff base) is depicted in Figure 20.

Ferrocenyl-bearing Schiff bases were reported to form CTs with iodine [263]. As to their polymer counterparts, ferrocene-containing poly(Schiff base) (Figure 21), poly[p-bis(ferrocenyl-Schiff base)], poly[m-bis(ferrocenyl-Schiff base)], and poly[o-bis(ferrocenyl-Schiff base)], were synthesized by Liu et al. [264] via condensation of ferrocenecarboxaldehyde with phenylenediamine, followed by reaction with a terephthaloyl chloride monomer. The poly(ferrocenyl-Schiff bases) were brown powders which upon doping with iodine in acetone solution, turned black. IR and UV-visible spectra of the undoped polymers changed at high iodine dopings, indicating a CT occurrence; in IR spectra, the absorption of Schiff base at around 1610 cm⁻¹ became less intense, and a new absorption band at 450–480 nm with a long tail extending to ~900 nm appeared in UV-visible spectra. The electrical conductivities of the iodine-doped poly(ferrocenyl Schiff base)s were measured to be in the range of $1.07 \times 10^{-5}$ to $5.48 \times 10^{-5}$ S·cm⁻¹ against $10^{-8}$ to $10^{-9}$ S·cm⁻¹ for bare poly(ferrocenyl Schiff base)s. In the same year, Xiong et al. [265] reported the synthesis and iodine treatment of poly[p-bis(ferrocenyl-Schiff base)] with about the same observation and characterization results as those of Liu et al. [266]. The iodine-doping extent increased with increasing amount of iodine and reached a plateau at ~0.4 g/g. The electrical conductivity
attained about $3.17 \times 10^{-4}$ S·cm⁻¹. Both workers imputed such a conductivity magnitude to the CTC formation between iodine and the lone pair of electrons of nitrogen atoms.

Farcas and Grigoras [266] came about with poly(Schiff base)s inserted into cyclodextrins, generating polyrotaxane-like materials (Figure 22). The synthesis involved a solution polycondensation of terephthaldehyde/α- or β-cyclodextrin adduct with 1,4-phenylenediamine. These polymers were more hygroscopic and more soluble in polar solvents such as DMF and DMSO. The conductivity of iodine-doped polymers was in the range of $10^{-7}$ to $10^{-6}$ S·cm⁻¹, compared with those of the pristine polymers (<$5.6 \times 10^{-9}$ S·cm⁻¹), and similar to those of other polymers non-containing rotaxane architecture.

### 2.2.3 Iodine carbon/hydrocarbon polymers complexes

Of the many hydrocarbon polymers, the unsaturated ones in particular, received much attention as far as complexation with molecular iodine is concerned. These include conjugated and unconjugated ones and are: the natural rubber (poly(cis-isoprene), polystyrene, styrene-butadiene rubber, polyacetylene, polyphenylacetylene, poly(phenylene vinylene), polybutadiene, graphite, carbon nanotubes, and fullerene C₆₀. Several conjugated polyenic naturally occurring molecules such β-carotene, β-apo-8’-carotenal, astacene, methyl bixin, lycopene, lutein, retinoic acid, vitamin A acetate, zeaxanthin, and fucoxanthin, were reported to develop CTCs with molecular iodine in the solid state [267–271]. A remarkable finding was that these iodine-treated molecules were endowed with high electrical conductivity, and were found, therefore, applications in solid state batteries [270, 278]; it increased with time of exposure to iodine vapors and reached a value of 38 S·cm⁻¹ (a conductivity at room temperature) for (CHI₀.22)x, the largest room temperature conductivity for an organic polymer known at that time. The iodine-treated PAC started to darken at an iodine content of 0.05 per carbon, suggesting a CTC formation. As to the cis-isomer, the conductivity was even higher than that of the trans-isomer, approximately one order of magnitude greater. Iodine in the form of the polyiodide $I₃$⁻ species in linear arrays was thought to exist in the iodine-cis-PAC [279]. Kaindl et al. [280] and Matsuyama et al. [281] showed the occurrence of both polyiodides $I₃$⁻ and $I₅$⁻ in linear shape by $^{129}$I Mössbauer analysis of iodine-doped cis- and trans-PAC, with an iodine content between 0.022 and 0.23 per carbon. The cis-trans isomerization of PAC, the cis being less stable, could be induced by doping with high concentrations with molecular iodine [282]. It was spectroscopically demonstrated that the iodine doping took place in the trans regions of the cis-isomer, either already present in the sample or created upon doping.
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[283]; strong absorption bands at 870 cm$^{-1}$ and 1390 cm$^{-1}$ appeared for the I$_2$-trans-PAC.

Guiseppi-Elie and Wnek [284] exposed cis-polyacetylene to iodine vapors in argon atmosphere. The extent of incorporated iodine into PAC was estimated to be 0.18 to 0.20 of iodine per CH. The conductivity of I$_2$-PAC was found to be in the range of 200 to 300 S·cm$^{-1}$ and to drop to 27% of its initial value after 9 days, even under inert conditions. This decay was rationalized in terms of the following reaction (Scheme 8).

However, highly iodine-doped PAC was stable in aqueous environments with accelerated decay kinetics in the presence of added nucleophiles such as halide and thiocyanide ions. In general, the decay increased with increasing nucleophilicity of the added nucleophile (I$^-$ > SCN$^-$ > Br$^-$ > Cl$^-$ > F$^-$). Iodine-doped PAC films were of poor thermal stability when heated between room temperature and 125°C in vacuo and the molecular iodine desorbed, leading to a decrease in electrical conductivity [285].

Poly(phenylacetylene) (PPAC), synthesized by refluxing phenylacetylene in benzene containing the catalyst [Rh(bipy)cyclooctadiene]PF$_6$ or [Pt(C=C-Ph)$_2$(PPh$_3$)$_2$], was doped with molecular iodine in chloroform [286]. With PPAC prepared with the platinum catalyst (molecular weight of about 1000), the [I$_3$]/[PPAC] molar ratio was ~1, and with the one prepared with the rhodium catalyst, the molar ratio was ~5. Raman spectroscopy revealed one band at 166 cm$^{-1}$ assigned to I$_2^+$ and two bands at 143 cm$^{-1}$ and 112 cm$^{-1}$, attributable to I$_3^-$. Far-infrared spectroscopy bands for these species were, respectively, 166 cm$^{-1}$, 143 cm$^{-1}$, and 86 cm$^{-1}$. This study showed that the polyiodide I$_n^-$, stemming from the reaction of I$_2$ with I$_3^-$, was the predominant species, regardless of the iodine concentration. Later, Furlani et al. [287] were interested in using iodine-doped polyphenylacetylene thin film (0.5–1.5 μm) as a humidity sensor; the PAC was the one made by the rhodium catalyst. The dependence of relative humidity on resistance characteristics was found to be approximately exponential and stable over more than a week of continuous use. The sensors showed good reversibility during dry/wet cycles and a fast response time.

Grigoryan and his collaborators [288] reported the polymerization of phenylacetylene and p-diethinylbenzene (PTDB) in the presence of iodine. The obtained polymers PPAC and PTDB were found to contain amounts of iodine species in a complex state, as formed by diiodo polycondensation (Scheme 9). The soluble PPAC, with a molecular weight of $M_n$=1320, bore 30.50% of iodine when the polymerization was conducted in benzene
Bakker and his group [290] reported the iodine doping of trans-rich oligo(phenyl acetylene) ($M_n=304 \text{ g/mol}$) film (600–700 nm thick), OPAC, that was deposited on a silicon wafer by the chemical vapor deposition technique. The film changed its colorless state to a yellow aspect. The peak at 700 cm$^{-1}$ of the FT-IR of undoped OPAC decreased in intensity after doping, and that of the peak at 1452 cm$^{-1}$ increased. The former is due to the out-of-plane bending of the Ph-C bond and the latter to the phenyl deformation parallel to the plane. This observation would indicate a strong interaction between iodine molecules and phenyl groups.

The emission analysis of the doped OPAC at 325 nm showed shifts to higher energies and an extra band appeared at 500 nm, which hinted at the interaction of iodine with the phenyl group.

PVC is reputed for its propensity to undergo dehydrochlorination, either thermally or chemically, to generate unsaturations within the matrix [291–294]. Guo et al. [295] transformed PVC ($M_n=93,900$) into polyacetylene-like polymers with long polyene sequences (about 27 sequences) (DPVC) via dehydrochlorination by KOH in THF and in the presence of PEO400 as phase transfer catalyst. The dehydrochlorination extent was about 78% after a time of 2 h with KOH/PEO treatment. The DPVC film was doped by immersion into iodine saturated CCl$_4$ solution for 1 h. The FT-IR spectrum of the iodine-doped DPVC was similar to that of iodine doped $\beta$-carotene, and its FT-Raman spectrum was identical to that of iodine-doped trans-polyacetylene. The doped DPVC showed electrical conductivity in the range of $1.2 \times 10^{-3} \text{ S cm}^{-1}$ to $2.1 \times 10^{-1} \text{ S cm}^{-1}$.

Goh et al. [273], Kyotani et al. [296], and Matsushita et al. [297, 298] invented a way to make helical polyacetylene and helical carbon and graphite films thereof. Helical polyacetylene (H-PAC) was obtained by polymerizing acetylene using the Ziegler-Natta catalyst, Ti(O-n-Bu)$_2$AIEt$_3$, dissolved in an asymmetric nematic liquid crystal (N-LC) composed of a mixture of $(S)$-1,1'-binaphthyl-2,2'-di-[$p$-(trans-4-n-pentylcyclohexyl)phenoxy-1-hexyl] ether, $p$-(trans-4-n-propylocyclohexyl)ethoxybenzene, and $p$-(trans-4-n-propylocyclohexyl)butoxybenzene. An SEM image of the formed polyacetylene showed a helical structure of a bundle of fibrils with one-handed screwed direction. Iodine doping of H-PAC was performed by exposing the polymer to iodine vapor at room temperature for 24 h. Polyiodide ions $I_3^-$ and $I_5^-$ were thought to be between the PAC chains, forming CTCs. The doped H-PAC film was then carbonized at 800°C using an electric furnace for 1 h under argon gas. The carbon film prepared was furthermore heated at 2600°C under flowing argon gas to yield graphitic film. X-ray diffraction (XRD) of the carbon film

![Scheme 9 In situ formation of iodine-poly(phenylacetylene) complex.](image-url)
prepared from the doped H-PAC at 800°C indicated no crystalline morphology. However, its Raman spectrum showed a strong and broad peak at 1350 cm⁻¹ (D-band) attributed to a disordered structure (amorphous state), together with a comparable peak at 1580 cm⁻¹ (G-band) corresponding to a graphitic structure (crystalline state). Networks of sp² hexagonal carbon bonds were formed during carbonization, as a result of hydrogen removal from H-PAC in the form of HI. The band at 1580 cm⁻¹ (G-band) became intense when the carbon film was further treated at 2600°C and the XRD spectrum indicated the occurrence of graphitic crystallization upon carbonization. The form of the graphitic product obtained at 2600°C had nearly the same helical structure of the carbon film and of the H-PAC (Scheme 10); this was termed “morphology-retaining carbonization method”. As may be noticed, the iodine doping prevented the H-PAC film from thermally decomposing at high temperature.

2.2.3.2 Iodine-poly(phenylene vinylene)

The second hydrocarbon conjugated polymer is poly(p-phenylene vinylene) or phen(p-phenene vinylene) (PPV) (Figure 25). It is reputed for its intrinsic conducting property and its oxidative and thermal solidity. Its numerous applications include organic light-emitting diodes (OLED) and photovoltaic devices, like transistors and lasers, because of its electroluminescent property and its electron-donating capacity. Besides these, this rigid-rod polymer is readily prone to doping for enhancement of some of its properties. Yet, much interest has been devoted to its derivatives, mainly the alkyloxy-substituted PPV with a long alkyl chain [299]. Iodine vapor treatment of PPV had a significant effect on its luminescence [300]; the iodine doping has provoked a new luminescent peak at 2.61 eV and quenched the initial one at 2.38 eV. In another report, PPV was exposed to iodine vapor in a sealed tube for 1 h at 90°C [301]. Infrared analysis of iodine-doped PPV showed new bands at 876 cm⁻¹, 1150 cm⁻¹, 1280 cm⁻¹, 1316 cm⁻¹, 1485 cm⁻¹, and 1550 cm⁻¹, attributed to the formation of quinoid units. Also, the UV-visible-NIR spectroscopy revealed, besides that of the pristine PPV at 367 nm, three new bands at 688 nm (1.81 eV), 1724 nm (0.73 eV), and 2292 nm (0.56 eV); the first band occurred at a higher energy. In comparison with the dopants FeCl₃ and H₂SO₄, the doping with iodine was reversible, and the weaker interaction of iodine with PPV was evidenced by the lower energy for the transitions inside the band gap. In addition, with iodine as dopant, a bipolaron (occurrence of two transitions with two positive charges) was demonstrated to form.

Khattab and Ahmed [302] prepared four PVPs from the Wittig reaction of the phosphonium salts of p-dibromomethylbenzene, m-dibromomethylbenzene, o-dibromomethylbenzene, and 1,4-dibromobutane with terephthaldehyde. The PVPs were doped via iodine vapor. The electrical conductivity was found to be dependent on the iodine extent; the higher the iodine amount, the greater the conductivity. Highest conductivity values at 25°C were in the order of phosphonium salt as 1.6×10⁻⁸ S·cm⁻¹ (1.3×10⁻¹¹ for the corresponding undoped PVP), 7.6×10⁻⁸ S·cm⁻¹ (2.4×10⁻¹¹ for the corresponding undoped PVP), 2.2×10⁻⁷ S·cm⁻¹ (5.2×10⁻¹¹ for the corresponding undoped PVP), and 8.9×10⁻⁹ S·cm⁻¹ for the PVPs at their highest iodine contents. The doping efficacy depended on the PVP structure, as did the conductivity; that of the corresponding dibromobutane was the lowest (8.9×10⁻⁹ S·cm⁻¹), hinting at its non-conjugation. However, those of the remaining ones were vinylene.
position-dependent; that is, the order of conductivity was \textit{ortho}-isomer\textgreater meta-isomer\textgreater para-isomer.

Curiously, in any of these reports, no indication of a possible color change was stated to provide an insight into a CTC.

\subsection*{2.2.3.3 Iodine-polybutadienic complexes}

\subsubsection*{2.2.3.3.1 Butadienic homopolymers}
Complexation of iodine with polybutadiene and poly(cis-isoprene) (natural and synthetic) and their copolymers, were investigated by many others. Russian workers \cite{303} investigated the reaction of high \textit{cis}-polybutadienes of molecular weights of \textit{2}\times\textit{10}^4 to \textit{2}\times\textit{10}^6 with molecular iodine in different organic solvents. An intensive absorption band at 305 nm in the UV spectrum was observed for a system consisting of added molecular iodine to a solution of polybutadiene in cyclohexane, hexane, CCl\textsubscript{4}, or CHCl\textsubscript{3}, indicating a CTC; this band disappeared upon applying the evacuation process to the iodine-polybutadiene complex. Also, this band was absent in the spectra of I\textsubscript{2} and polybutadiene taken in these solvents. In CCl\textsubscript{4}, the complexation occurred in a 1:1 ratio. Of note was the band at 275 nm, which appeared when I\textsubscript{2}-polybutadiene in CCl\textsubscript{4} was exposed to light for a period of time, and did not disappear upon evacuation, suggesting a different form of complex between iodine and polybutadiene. However, in benzene solution and at 25°C, the iodine content did not exceed 21%. IR spectra showed characteristic bands of the C-I bond at 555 cm\textsuperscript{-1}, 580 cm\textsuperscript{-1}, and 640 cm\textsuperscript{-1}, stemming from the addition of I\textsubscript{2} to double bonds. Henceforth, the mechanism of addition of I\textsubscript{2} to polybutadiene was proposed as in Scheme 11.

According to Thakur \cite{304} and Dai and White \cite{305}, the color formation claimed by the Russians as a result of CT is unlikely to happen, as no conjugation is possible with \textit{cis}-polybutadiene at room temperature. Dai et al. \cite{306} reported that the treatment of \textit{cis}-1,4-polybutadiene with molecular iodine at room temperature stopped at the addition stage.

In 1988, Thakur \cite{304} announced an unprecedented claim, which consisted of the high electrical conductivity of non-conjugated polymers (Figure 26) but with appropriate substituents within the backbones. He investigated the conductivity of I\textsubscript{2}-\textit{cis}-poly(butadiene), I\textsubscript{2}-poly(2,3-dimethylbutadiene), and I\textsubscript{2}-poly(1,4-isoprene). Neither the color nor the conductivity (\textit{\approx}10\textsuperscript{-13} S·cm\textsuperscript{-1}) changed when polybutadiene was treated with iodine, whereas poly(2,3-dimethylbutadiene) and poly(1,4-isoprene) (synthetic and natural rubber, \textit{cis} and \textit{trans}) turned black upon such treatment. The electrical conductivity of the iodinated polyisoprene was around 10\textsuperscript{-2} to 10\textsuperscript{-1} S·cm\textsuperscript{-1}, that is, 10 orders of magnitude greater than that of the pristine one (\textit{\approx}10\textsuperscript{-13} S·cm\textsuperscript{-1}). Also, it was found that the rate of iodine doping of poly(2,3-dimethylbutadiene) was larger than that for poly(1,4-isoprene), probably due to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme_11.png}
\caption{Mechanism of the iodination of polybutadiene.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_26.png}
\caption{(A) Poly(cis-1,4-butadiene), (B) poly(trans-1,4-butadiene), (C) poly(trans-isoprene), Balata rubber, (D) poly(cis-isoprene), Hevea rubber, (E) poly(2,3-butadiene).}
\end{figure}
the disubstitution. The electrical conductivity of poly(1,4-

isoprene) reached a maximal value for 65% content of

iodine per isoprene unit. It was first thought due to the

inductive effect of the methyl substituent, being an elec-

tron-releasing group. This proposal was dismissed and it

was then proposed that radical cation polaron formation
(Figure 27) would be responsible for such an increase in

conductivity, and the electrons move through the inter-

chain hopping. In an FT-IR spectrum of the iodine-doped

poly(cis-isoprene), the band at 836 cm$^{-1}$ of $\equiv$C-H decreased

rapidly and a new band appeared at 1545 cm$^{-1}$ while the

$\equiv$C=C- stretching mode at 1673 cm$^{-1}$ disappeared as a conse-

duence of doping. The new band at 1545 cm$^{-1}$ was assigned

to the radical cation (Figure 27A) that is formed upon CT.
The decrease in the concentration of double bonds upon

iodine doping, in favor of radical cations, was also con-

firmed by CP/MAS NMR data [307].

However, Suh and Wneck [308] observed a new peak

at 1490 cm$^{-1}$ for the iodine-doped poly(3,4-isoprene) (70%

rich in 3,4-units), and was attributed to the iodonium

complex (Figure 27B). Indeed, when poly(3,4-isoprene)

was exposed to iodine vapor for 48 h at 25°C, the FT-IR

bands at 3100 cm$^{-1}$ ($\equiv$C-H stretching), 1640 cm$^{-1}$ ($\equiv$C=

stretching), and 980 cm$^{-1}$ (C-H out-of-plane deformation),

completely disappeared, and no ESR signal was detected,

hinting at the absence of a radical. Only the $\mathrm{I}_3^-$ species

was observed by means of UV-visible analysis, by the

appearance of two bands at 290 and 350 nm. Its conduc-

tivity increased with time of exposure to iodine vapor and

 leveled off at a value of $\sim 10^{-3}$ S·cm$^{-1}$ after 24 h.

Such peculiar findings triggered a spate of investiga-

tions. Indeed, Dai and White [305], Dai et al. [306, 309] and

Dai [310] embarked in deciphering the origins of Thakur’s

discovery. Stable sequences of conjugated double bonds

were generated in poly(1,4-isoprene) and in poly(trans-

1,4-butadiene), through double bonds shifting, upon

iodination in the solid state at room temperature. The

highly electrical conductivity and the color change of the

thus-iodinated soluble poly(1,4-isoprene) were rational-

ized in terms of such a conjugation and thus creating pol-

yacetylenic-type regions within the polymer matrixes. A

mechanism of such a phenomenon was proposed as given

in Scheme 12. In contrast, the iodine doping of poly(cis-

1,4-butadiene) at room temperature did not produce

such conjugation sequences, probably due to an unfa-

vorable combination of electronic and steric interactions

coupled with the polymer backbone geometry. Dai et al.

[306] imputed the behavior difference between the two

isomeric polymers to intramolecular properties, rather

than the intermolecular packing, and suggested that the

actual doping be better termed “an iodine mediated con-

jugation reaction”. However, it was possible to create this

conjugation by either photoirradiating iodinated poly(cis-

1,4-butadiene) or isomerizing poly(cis-1,4-butadiene) into

poly(trans-1,4-butadiene), by exposure to UV irradiation

in the presence of a photosensitizer such as diphenyl

disulfide, followed by iodine doping [311], or by heating

the iodine-doped poly(cis-1,4-butadiene) at 60°C for a time

longer than 22 h [306]. The heat-induced conjugated

$\mathrm{I}_2$poly(cis-1,4-butadiene) was then found to develop CTC

involving long polyene sequences. Also, such conjuga-

tion formation in non-conjugated hydrocarbon polymers

occurred in the solid state as well as in solution (toluene

and cyclohexane).

Dai [310] demonstrated such conjugation formation by

an elegant experiment of a two-phase system. It involved

mixing a CCl$_4$ polyisoprene solution with an I$_2$-saturated

methanol solution, and equilibrating the two phases

immiscibly. The CTC formation was easily and advanta-
geously monitored by UV-visible spectroscopy, showing a

color change from colorless to pale yellow and then dark

brown. It was noted that the $\mathrm{I}_3^-$ species was detected in the

CTC by the bands appearing at 292 nm and 358 nm.

Shang et al. [312] prepared poly(trans-butadiene)

and poly(trans-2,3-dimethylbutadiene) through inclusion

polymerization of their corresponding monomers. The

two polybutadienes, in the form of pressed pellets, were

treated with iodine vapor overnight. Both doped polymers

became metallic black in color; poly(trans-butadiene)

changed color more rapidly than poly(trans-2,3-dimethyl-

butadiene). The presence of $\mathrm{I}_2$ and $\mathrm{I}_3^-$ was evidenced by

far-infrared analysis; three bands at 137 cm$^{-1}$, 104 cm$^{-1}$, and

44 cm$^{-1}$ for the former species and one weak band at 163 cm$^{-1}$

for the latter one. The authors suggested the formation

of an iodonium-$\pi$ complex, together with the formation

of iodine species as shown in Scheme 13. The electronic

conductivities were $1 \times 10^4$ S·cm$^{-1}$ and $3.5 \times 10^{-4}$ S·cm$^{-1}$ for

poly(trans-butadiene) and poly(trans-2,3-dimethylbuta-

diene), respectively. The authors believed that the effect

of methyl substituents in terms of color change and con-
ductivity upon treatment with iodine, may be related to

differences in packing in the solid state rather than being

related to unimolecular properties, influencing the iodine

permeability and affecting the nature of the complex

formed.
Seto et al. [313] demonstrated the iodine species in the doped poly(trans-isoprene) by means of Mössbauer resonance of 129I. Doping was made by exposure of a polyisoprene film to 129I2 vapor in an argon atmosphere. It was concluded that at a low doping level (C 5H8I0.02), most of the iodine species were bound to carbons of the polymer backbone by attack of the double bonds, and at high dopings (C5H8I0.17), they existed in the forms of the I3− and I5− species in addition to the covalently bonded ones. At a higher iodine level (C5H8I0.77), I5− and I2 were the predominant species in the polyisoprene complex.

Shi and his co-workers [314] synthesized polybutadiene with a molecular weight of 6800–12,000 and with high trans microstructure (97–98%), and the polymer film was then doped with iodine vapor at 30°C. The doping engendered a color change from white to dark-gray. The highest doping level was found to be 62–65% after 24 h of exposure, giving rise to a conductivity of 10⁻³ S·cm⁻¹. This conductivity was shown to be molecular weight dependent, that is, 9.9×10⁻⁴ S·cm⁻¹ for polybutadiene (Mₙ=6800), and 1.1×10⁻³ S·cm⁻¹ for polybutadiene (Mₙ=12 000).

Chilkoti and Ratner [315] proved, by X-ray photoelectron spectroscopy (XPS) studies of iodine-doped poly(cis-butadiene), and poly(trans-isoprene), the occurrence of Thakur’s radical cation and disproved the iodonium cationic complex [308, 312]. To one’s surprise, these authors were able to dope poly(cis-butadiene), disapproving Thakur’s result [304]. The XPS analyses at a low temperature (-80°C) affirmed that the electronic conductivity was due to excess iodine in forms of molecular iodine and I⁻ and I₃⁻.

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**Scheme 12**  Mechanism of the iodination of polydiene proposed by Dai. Reprinted with permission from Ref. [310]. Copyright (1992) American Chemical Society.

**Scheme 13**  Formation of polyiodide ions from molecular iodine and of iodonium-π complex. Reprinted with permission from Ref. [312]. Copyright (1990) American Chemical Society.
The report of Owen and Al-Moh’d [316] on iodine-doped poly(cis-isoprene) confirmed the disappearance of the FT-IR bands at 1664 cm\(^{-1}\) and 835 cm\(^{-1}\) and the appearance of a new band at 1599 cm\(^{-1}\) as seen by Thakur [304]. Owen’s result, via fluorescence emission and excitation spectroscopy analyses, put forward the double bond shifting, suggesting a synergism of the radical cation (Thakur) and the iodonium complex [308, 312].

In the course of investigating the effects of iodine-doping on the dielectric and thermal properties of vulcanized natural rubber (cis-polyisoprene), Da Silva and Miranda [317] also observed the occurrence of conjugation formation. Optical absorption analysis illustrated that the absorption edge shifted towards longer wavelengths as the iodine-doping concentration increased, in accord with the darkening color of the sample. Two new FT-IR bands at 1545 cm\(^{-1}\) and 1605 cm\(^{-1}\) appeared upon doping, as disclosed by other workers [304, 310, 312]; the absorption coefficients of these bands increased with increasing iodine doping and those of the bands at 836 cm\(^{-1}\), 930 cm\(^{-1}\) decreased. An electrical conductivity of higher than 10\(^{-9}\) S·cm\(^{-1}\) was measured for an iodine concentration of 16 g/l and after an aging period of 5 days. Doping natural rubber with 6 g/l concentration of iodine, and after this period, the sample showed a dielectric constant (\(\varepsilon\)) of 19.2, that is, eight-fold greater (pristine rubber \(\varepsilon=2.35\)). Thermal diffusivity, defined as \(\alpha=κ/ρC\) (\(κ, ρ,\) and \(C\) are thermal conductivity, density, and heat capacity, respectively) was the thermal property studied in this work and measured by a photoacoustic technique. The results showed that at low doping levels, the thermal diffusivity went down by increasing the doping concentration up to 6 g/l, beyond which the thermal diffusivity exhibited a sharp growth at high doping concentrations, reaching saturation at \(α\sim1.1×10^{-3}\) cm\(^2\)/s for a dopant concentration of 20 g/l. The elastomer modulus of rubber jumped from 4.3×10\(^3\) to 3.04×10\(^8\) Pa when doped with an iodine concentration of higher than \(-12\) g/l.

Nisha and Joseph [318] designed a radiopaque material by iodinating natural rubber (INR), for use in medicine and dentistry because of the wide area of applications such as catheters, surgical tools, dental products, and medical tubings. INR samples showed a great thermal stability; its decomposition started at about 331°C and the DTG curve showed a maximum degradation peaked at 444°C. INR film of high thickness and cured at a low temperature gave better radiopacity. Theoretical calculations demonstrated that the conductivity of iodine doped poly(cis-1,4-isoprene) resulted from the conduction of both parallel and perpendicular to the chain direction, the conductivity of interchain being higher than that of intrachain [319]. Also, polyiodides I\(^{–}\)\(_n\) were the dominant contributors to the conductivity in parallel to the chain direction, while both I\(^{–}\)\(_n\) species and double bonds of interchains contributed to the conductivity in the perpendicular direction.

To combat the adherence of bacteria during the pathogenesis of catheter-associated urinary tract infection, Mazumdar and his co-workers [320] iodinated the latex poly(cis-isoprene)-made catheters with molecular iodine at room temperature, for a time ranging from 2 to 30 min. The iodinated catheters were colored from light brown to black brown, depending on the exposure time. The results were that such iodinated materials with 1.49–2.93% iodine had good antibacterial activity for a week against \(E. coli\), \(S. aureus\), \(K. pneumoniae\), \(P. aeruginosa\), \(Enterococcus\), \(faecalis\) and \(S. epidermidis\).

### 2.2.3.3.2 Butadienic copolymers

Iodine doping of butadiene copolymers such as styrene-butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR), acrylonitrile-butadiene-styrene (ABS), and butadiene-2-vinylpyridine copolymer, was also studied. Stanković et al. [321] prepared diblock copolymer of butadiene and 2-vinylpyridine \((MN=25\times10^3\) to \(225\times10^3\)), and the butadiene fraction in the copolymer=63–87%) via anionic polymerization and treated the copolymer film with iodine vapor at room temperature. In general, the doping rate for the highest electrical conductivity of the copolymer was about 3 weeks, a time thought to be relatively short, which was imputed to the easy penetration of iodine molecules within the polybutadiene phase. These copolymers with different compositions and morphologies absorbed the same amount of dopant (75–78%) and had about the same electrical conductivity at room temperature \((2.9×10^{-4} S\text{-cm}^{-1}\) to \(1.4×10^{-3} S\text{-cm}^{-1}\)). The authors judged the high conductivity of the doped copolymers as due to iodine itself and the CTCs formed with polybutadiene and poly(2-vinylpyridine) blocks served merely as conducting impurities.

Ramani et al. [322] and Ramani and Ranganathaiah [323] investigated the iodine sorption by ABS resin, employing positron annihilation lifetime spectroscopy (PALS). Iodine sorption was performed by soaking the sample in an aqueous I\(_2\)/KI solution for different time intervals at room temperature. The average free-volume size of ABS was 106 Å, as determined by PALS analysis and, consequently, the predominant polyiodide species would be I\(^{–}\)\(_n\) that filled the holes of the ABS resin because its size (104 Å) fitted well. The authors concluded that the sorption or CTC took place more favorably in the crystalline
region and crystalline/amorphous interface of the resin, and the CTC occurred more probably at the phenyl sites of the styrene units, although such CTC is weak. The diffusion of iodine species through ABS was found not to obey Fick’s law, and the dependence of the free volume on the diffusion coefficient did not follow Fujita’s theory.

Sreeja et al. [324] studied the impact of iodine doping on the properties of acrylonitrile butadiene rubber (NBR, molecular weight of $1.8 \times 10^5$ and butadiene content of 73%). The doping procedure was either by keeping a chloroform solution of a mixture of an NBR sample and iodine under argon at room temperature and for different times (solution state) or by exposure of NBR film to iodine vapors (solid state). The conjugation phenomenon was found to happen in this case and the colorless starting material became pale yellow-dark to yellow-red with increasing doping period. In the optical absorption spectrum, two new and broad bands appeared between 300 nm and 500 nm with increasing intensity as the doping period was prolonged, and the band at 262 nm, attributable to isolated C=C bonds, decreased. Also, the FT-IR spectrum indicated a decrease in intensity of the characteristic band of C=C bonds (1650 cm$^{-1}$) and the appearance of new bands at about 1540 cm$^{-1}$, assigned to a conjugation. The band of the nitrile group (2236 cm$^{-1}$) remained, however, unperturbed by doping, as the CTC between the nitrile group and iodine is weak. The electrical conductivity of NBR increased by eight orders of magnitude with doping time increasing, attaining a maximum value of $10^{-2}$ S·cm$^{-1}$ after about 58 days, a doping time longer than that for the homopolydienes discussed above.

Telang and Thakur [325] and Titus et al. [326] disclosed the electrical conductivity, the mechanical properties, and the electro-optic effects of the iodine-doped SBR, a non-conjugated hydrocarbon material. A color change from colorless to black was seen. The intensity of the IR bands of =C–H (964 and 910 cm$^{-1}$) decreased upon doping, hinting at the interaction of iodine with the isolated double bond, which led to a CTC and the polaron creation (radical cation). An optical absorption spectrum indicated the occurrence of both phenomena at 4.27 and 3.2 eV, respectively. The electronic conductivity attained $10^2$ S·cm$^{-1}$. The Kerr coefficients were measured to be $3.1 \times 10^{-10}$ and $1.3 \times 10^{-10}$ m/V$^2$ at 633 and 1550 nm, respectively. The polystyrene segments of the copolymer had less interaction with iodine because of their glassy state, and the phenyl group developed a weak CTC with iodine.

Recently, Thakur [327] patented his findings that consisted of the faster sulfur vulcanization of unconjugated hydrocarbon polymers in the presence of iodine, giving rubbery materials. Such polymers included polyisoprene, poly(cis-1,4-butadiene), ethylene-propylene-diene monomer (EPDM), styrene-butadiene copolymer (SBR), and poly(β-pinene). Mechanical properties of thus-cured polymers were markedly enhanced, even without fillers. For example, the modulus of poly(cis-isoprene) rose from $\sim$13 to $\sim$53 MPa upon curing under this strategy, and that of SBR increased from $\sim$30 to $\sim$53 MPa. The mechanical properties of SBR were enhanced on doping; its modulus which was low ($\sim$30 MPa) became $\sim$153 MPa, and the elastomeric property could be improved by removing the residual iodine with hexane.

### 2.2.3.3 Other polyenes

**Treatment of poly(β-pinene)** (Figure 28A), a non-conjugated hydrocarbon polymer, with iodine vapor at room temperature was performed by Vippa et al. [328]. The polymer was saturated with iodine at a level of 85% and became a dark-colored substance. The electrical conductivity of the I$_2$-poly(β-pinene) was measured to be $\sim 8 \times 10^{-3}$ S·cm$^{-1}$, that is, an increase of about 10 orders of magnitude (the conductivity of undoped poly(β-pinene) was $\sim 10^{-12}$ S·cm$^{-1}$). Optical absorption analysis of the undoped film showed a very weak band at 280 nm, and that of the lightly doped film showed two peaks: 310 nm (4.0 eV) and 400 nm (3.1 eV). The first band (4.0 eV) was attributed to a radical cation (Figure 28B), and the second peak (3.1 eV) to a CT between the double bond and I$_2$. This second band broadened and underwent a red shift at higher doping levels. By the same analysis, a poly(ethylenepepyrolediyli) derivative was found to develop a radical cation when doped with iodine [329]; the two corresponding peaks appeared at 310 nm (4.0 eV) and 420 nm (2.95 eV).

The intensities of IR bands of poly(β-pinene) at 1610 and 728 cm$^{-1}$ decreased upon higher iodine doping, a result that was consistent with the conversion of the double bonds into radical cations (Figure 28B). Upon doping with

![Figure 28](image-url) (A) Poly(β-pinene), (B) polaron in case of poly(β-pinene).
iodine, the emission band in the photoluminescence spectrum of the polymer that appeared at 380 nm upon excitation at 280 nm was substantially reduced. Similar results were obtained for iodine-doped poly(cis-isoprene) [330], confirming the formation of radical cations (polarons).

As to the spectral evidence of the radicals, Narayanan et al. [331] and Thakur and Elman [332] proved their existence by EPR measurements of iodine-doped poly(β-pinene) and poly(cis-isoprene) in powder form. While the undoped poly(β-pinene) sample showed a very weak EPR signal due to the methyl radicals, significant EPR signals increasing in proportion to the iodine concentration were observed with a g-value of 2.0042 and EPR line-width of 13 G (Figure 29).

Non-linear optical properties of iodine-doped poly(β-pinene), such as the quadratic electro-optic effect (or Kerr effect) and the two-photon absorption coefficients ($\alpha_2$) were measured [333–336]. The maximum $\alpha_2$ was obtained at about 2.6 cm/MW, and the Kerr coefficient was determined to be $1.6\times10^{-10}$ m/V$^2$ at 1.55 µm. The magnitudes of the non-linear optical effects (Kerr coefficient and $\alpha_2$) for the iodine-doped poly(β-pinene) were exceptionally large. A similar study on poly(trans-isoprene) gave a Kerr coefficient of $2.5\times10^{-10}$ m/V$^2$ at 1.55 µm [337] or $1.2\times10^{-10}$ m/V$^2$ at 633 nm [333]; that is, 50 times that of nitrobenzene. The observed nonlinearities have been attributed to the subnanometer-size metallic domains termed as “quantum dots”, formed upon doping and charge transfer in this non-conjugated conductive hydrocarbon polymer.

A very interesting remark was that the electrical conductivity of the polyenes rose with the double bond number fraction (the number of double bond over the number of bonds in the polymer unit) as illustrated in Table 1.

### Table 1: Electrical conductivities of non-conjugated conductive hydrocarbon polymers with different double-bond fractions [329].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Double-bond number fraction</th>
<th>Electrical conductivity (S·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(β-pinene)</td>
<td>1/6</td>
<td>$8\times10^{-3}$</td>
</tr>
<tr>
<td>Polynorbornene</td>
<td>1/5</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>cis-Polyisoprene</td>
<td>1/4</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>Polyalloocimene</td>
<td>1/3</td>
<td>1</td>
</tr>
<tr>
<td>Polycetylene (conjugated</td>
<td>1/2</td>
<td>100</td>
</tr>
<tr>
<td>hydrocarbon polymer)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


2.2.3.4 Iodine-carbon nanotube/ fullerene complexes/ graphite

Graphite is an allotropic form of carbon with a layered and planar structure (distance between the planes=0.335 nm) in which the carbon atoms are arranged in fused benzene rings (carbon carbon bond distance=1.415 nm) (Figure 30). A theoretical study on the aromaticity of the graphite revealed that it is a limit in the polycene series [338, 339]. Graphene is also an allotropic form of carbon, with a monolayered structure (carbon carbon bond distance=1.42 nm) (Figure 30); the crystalline form of graphite consists actually of stacked graphene sheets.
One feature of the graphite, and owing to its layered structure, is its ability to host atomic and molecular species via intercalation [340, 341]. A theoretical investigation of the adsorption of halogens (F₂, Cl₂, Br₂, I₂) on graphene was undertaken [342] using a van der Waals density functional theory (vdW-DFT). The results indicated that the adsorption mechanism is actually governed by van der Waals and electrostatic interactions, particularly for F₂ and I₂; the ionic nature of the interaction arose due to the electronic transfer from graphene to the halogen molecules. 

A very important outcome was that the densities of states for graphene in the presence of Br₂ and I₂ molecules exhibited impurity bands right above the Fermi level, which can result, for a large enough concentration, in the metallization of graphene, which may explain the enhancement of the electrical conductivity of graphene by iodine doping.

When a mixture of graphite and molecular iodine in a ratio of 4:1 was heated at elevated temperatures, from 100 to 1000°C, the iodine-treated graphite taken as a cell anode in lithium batteries showed a superior electrochemical performance [343]. The temperature seemed to play a critical role in such performance. Particularly, treatment at 700°C led to a great extent of iodine species chemically bonded on the electrode surface, improving the building up of solid electrolyte interface (SEI) which thought to be the key factor of a good performance. Cyclic voltammetry studies confirmed such findings. Conducting carbon films were produced by vapor phase pyrolysis (700–980°C) of maleic anhydride in the presence of molecular iodine, followed by annealing of the product for 5 h under argon atmosphere [344]. The product was conducting, shiny, light grey in color and contamination-free. Its electrical conductivity increased with an increase in iodine concentration; for an iodine-saturated sample, the conductivity was about nine times that for zero iodine (∼900 S·cm⁻¹ vs. ∼100 S·cm⁻¹). Also, it was observed that, at low temperatures, its conductivity measured at fixed field (7 T) decreased drastically compared to the sample at 0 T, indicating a magnetic field-induced metal-insulator (M-I) transition.

Polyiodides I₃⁻ and I₅⁻ as strong peaks at 108 cm⁻¹ and 165 cm⁻¹ in the Raman spectrum were detected when some graphene layers were exposed to iodine vapors [345, 346]; a peak of weak intensity appeared at 212 cm⁻¹, assigned to I₂. As with graphite, molecular iodine was not found to intercalate between the graphene sheets, but to be adsorbed on the top and the bottom, as the Raman spectra would suggest. From Raman signals and with the means of hole density measurement, it was possible to estimate the number of polyiodides present on the surface to be 1.3×10¹⁵/cm², that is, one iodine anion per adsorbed layer for every 300 graphene C atoms (the graphene carbon atom density was 3.8×10¹⁵/cm²). By contrast, iodine-doped graphene was prepared in situ by pyrolyzing a mixture of camphor and molecular iodine at a ratio of 2:1 (Scheme 14) at 800°C under argon atmosphere [347]. The Raman graphic bands (1347 cm⁻¹ and 1587 cm⁻¹ for D and G bands) of the graphene were not altered upon iodine-doping, indicating that sp² hybridization of the carbon was not disturbed (Figure 31). The peaks corresponding to I₃⁻ and I₅⁻ were apparent at 117 cm⁻¹ and 154 cm⁻¹, respectively; the intensity of the triiodide anion peak was stronger than that of the pentaiodide one. The authors believed that molecular iodine was absent as an expected peak at 181 cm⁻¹, yet the band observed at about 225 cm⁻¹ was not discussed. In addition, the XPS analysis proved that the iodine atoms were introduced via carbon atoms and not as pure iodine molecules, and indicated a CT reaction between iodine and carbon atoms. This analysis revealed 3.1% atoms of iodine were incorporated within the graphene sheets. The polyiodide anions were present on the surface of the graphene layer and within the intercalation zones as confirmed by in-depth XPS profiling studies.

Yao et al. [348] prepared iodine-doped graphene by annealing graphene oxide (GO) and iodine at 500–1100°C in argon at an adjusted GO/I₂ mass ratio. XPS characterization of iodine-graphene resulting from the reaction at 900°C, revealed the existence of I₃⁻ and I₅⁻ as two adjacent peaks, 618.6 and 620.2 eV, respectively. Raman spectroscopy showed the G band at 1594 cm⁻¹ and two new Raman

![Scheme 14](https://example.com/scheme14.png)  *In situ* iodine doping of graphene.
peaks at 117 cm⁻¹ and 154 cm⁻¹, corresponding bands of the polyiodides, and the characteristic band (181 cm⁻¹) of the molecular iodine was absent. The thus-made iodine-graphene exhibited an electrocatalytic property in oxygen reduction reactions (ORR) superior to that of the commercial Pt/C catalyst, and showed longer stability. This material was claimed to be a non-noble metal catalyst (NPMC), and the I₃⁻ species played a crucial role for enhancement of the ORR activity of graphene.

One of the synthetic carbons is the diamond-like carbon (DLC), which exists in several forms, the sp³ containing one being the most common. The latter form, also called polycarbyne (CR)n (Figure 32A), can be made electrochemically by subjecting a solution of RCX₃ (R=alkyl, phenyl, H; X=halogen) to an electrical current in the presence of electrolyte [349], or in the presence of Na-K amalgam and under ultrasound conditions [350]; the diamond-like carbon was tan-colored with a molecular weight of $M_w \sim 4000$. Omer and his collaborators [351] studied the effect of iodine doping on the optoelectronic properties of DLC thin films. The latter films were produced on a silicon substrate by applying the microwave surface wave plasma chemical vapor deposition (MW SWP CVD) to methane or camphor at a temperature of lower than 100°C. Doping was processed by subjecting the thin film to iodine vapors. The optical bandgap of the iodine-doped films was narrowed to 1.9 and 0.5 eV before and after annealing, respectively. However, the results obtained by Allon-Alaluf and Croituru [352] were 1.1 and 0.78 eV for amorphous DLC and the iodine-doped one, respectively. The resistivity of the doped one dropped by about four orders of magnitude, about $4.0–6.0 \times 10^4$ Ω-cm for iodinated DLC (20% iodine partial pressure) against $1.4 \times 10^8$ Ω-cm for the pristine a:DLC.

Polynes H-(C≡C)ₙ-H with n=5, 6, and 7 (Figure 32B), prepared by laser ablation of graphite particles, were complexed with molecular iodine in dark and in hexane solution [353]. Photoirradiation of the complex in hexane induced a dramatic change in the NMR (¹H and ¹³C) and UV-visible spectra, as typically shown in Figure 33. NMR peaks were shifted to the lower field, and the coupling constants were reduced. UV-visible spectrum revealed the disappearance of the bands of the polynes (252 nm, 239 nm, and 228 nm for n=5) and the emergence of new bands (316 nm, 336 nm, 361 nm, and 390 nm for n=5). Such analyses indicated that the conjugated carbon chain of the undoped polyyne was retained after iodine treatment. Irradiation was required to promote the complex formation and it was found that the stoichiometry was [polyyne]/[I₂]=1/3. Based on the NMR characterization, the iodine-polyyne complex was neither a substitution nor an addition product of iodine atoms. Decomplexation was possible by irradiating the complex with visible light, and the spectral patterns of the polynes were restored, suggesting a reversible reaction.
Fullerene $C_{60}$ (Figure 34A) and carbon nanotubes (CNTs) (Figures 34B and C) are considered carbon polymers, consisting of only carbon atoms. They have been exploited as dopants for conducting polymers to enhance their photoconductivity [354]. Because of its high ionization potential (7.6 eV), fullerene $C_{60}$ is expected not to interact with molecular iodine under no external force. Indeed, some reports indicate the weakness of this interaction [355–357]. However, some molecules of about the same ionization potential such as pyrene (7.41 eV) and perlyene (7.00 eV) do act as electron donors towards molecular iodine [358, 359]. The reaction between fullerene $C_{60}$ and molecular iodine was first made by Kobayashi and his collaborators [360]. The procedure consisted of sealing excess iodine with $C_{60}$ powder under helium gas (10 Torr) in a reaction tube. The tube was then placed in an electric furnace at constant temperature. The reaction was followed in situ by measuring the change in powder X-ray diffraction profile and $ac$ magnetic susceptibility. The solid compound ($C_{60}I_x$) was colored to dark when heated and was stable in air. The compound contained four iodine atoms per fullerene molecule, and each iodine atom was incorporated into a trigonal prism formed by six fullerene molecules. Its superconductivity was not detected down to 4.2 K. The stability of the $I_2C_{60}$ complex was found to decrease with pressure up to 27 GPa, beyond which it increased slightly [361]. Znner and Zabel [355] observed that heating a sublimed mixture of $C_{60}$ and an excess of iodine at 130°C for 20 h failed to produce an $I_2C_{60}$ complex, as proved by XRD analysis. However, irradiation of the mixture by Hg light gave a product whose X-ray profile was completely different from that of the pristine $C_{60}$. It was believed that the irradiation by Hg light would fragment iodine molecules into iodine radicals. The XRD spectrum suggested an intercalation of iodine atoms within $C_{60}$ molecules.

Treatment of the fullerene by an excess of molecular iodine in a furnace at a temperature of 200–400°C for few hours, resulted in polymeric $C_{60}$ aggregates with formula of $C_{60}I_x$ ($x=0.2–1.5$), forming free-standing foils [362]; the product was a mixture of hexagonal and face centered cubic forms. Interesting, was that the skeleton of $C_{60}$ retained its $Ih$ symmetry upon such a treatment. However, the $C_{60}I_x$ samples were stable at ambient conditions and, in contrast to the virgin $C_{60}$, were insoluble in toluene and did not sublime upon heating to 350°C in a dynamic vacuum. Also, the iodinated $C_{60}$ samples were found to be diamagnetic and electrically highly insulating, and to exhibit magnetic transition around the temperature of 60°C. Raman spectroscopy of the iodine intercalated $C_{60}$ crystals was studied at a temperature range of 13 to 300 K [363]. At 13 K, three distinctive bands were present at 167 cm$^{-1}$, 183 cm$^{-1}$, and 198 cm$^{-1}$, the first band being the strongest. All three bands were lower than that of $I_2$ (213.3 cm$^{-1}$) and higher than that of $I_3^-$ ($≈107$ cm$^{-1}$). These bands tended to broaden with increasing temperature until their complete disappearance at 300 K. The first two bands (167 cm$^{-1}$ and 183 cm$^{-1}$) were assigned to stretching vibrations for two different molecular species existing in the iodine molecular chain, and the difference in their intensities was thought to be due to the differences in bond length and intramolecular CT of iodine molecules. The last band (198 cm$^{-1}$) was tentatively attributed to the vibration of isolated $I_2$ molecules.

Zhu and his co-workers [364] also prepared iodine-doped fullerene $C_{60}$ by vapor phase reactions (at 250°C for several days in evacuated Pyrex tubes). A single stable phase, having more than three iodine equivalents per $C_{60}$, was observed for all samples as revealed by X-ray diffraction measurement; a formula of the complex would be as $C_{60}(I_2)_x$.

Turtanov and Kremenskaya [365] investigated the interaction of fullerene $C_{60}$ with molecular iodine in a ratio...
of 1:3 in a two-phase medium (organic solvent: water, 1:1), at 20°C for 1 h. A color change was observed, indicating the occurrence of the complexation. Adduct \( \text{C}_{60}\text{I}_3 \) was claimed to form in toluene, benzene, xylene, chloroform, and hexane. Surprising, was that the solubility in chloroform increased with increasing iodine concentration. The constant of the formation of \( \text{C}_{60}\text{I}_3 \) was estimated to be 8.9. The results, mainly confined to the stability of the \( \text{C}_{60}\text{I}_3 \) complex and the solubility dependence of \( \text{C}_{60} \) on iodine concentration, were disapproved by Beck et al. [356, 366]. The latter authors [366], however, proved spectrophotometrically the formation of a complex, and thermogravimetrically the covalent binding of some part of iodine.

Berdinsky et al. [367] prepared films made of \( \text{C}_{60} \) and iodine for sensor electronics. This was possible by mixing them in a chamber at 510°C, followed by deposition onto a cooled substrate. The formula of the compound was established as \( \text{C}_{60}\text{I}_x \). The electrical resistance of the designed film and its temperature dependence were different from those of the pure \( \text{C}_{60} \) fullerene film; iodine caused a sharp decrease of the film resistance down to \( 10^{5}–10^{6} \ \Omega \) at room temperature (that of pure fullerene is \( 10^{10}–10^{12} \ \Omega \)). The resistance of the iodine-doped \( \text{C}_{60} \) declined within the temperature range of \( \sim 50–80°C \), and went up afterwards. At temperatures above 80°C, iodine was sublimed off the sample and the resistance increased.

Grigorian et al. [368] doped single wall carbon nanotube (SWNT) (Figure 34B) with molten iodine at 140°C for several hours. The \( \text{I}_2\text{-SWNT} \) was air stable. Upon this iodine doping, the crystalline lattice shifted to lower angles and finally disappeared, as evidenced by XRD measurements, suggesting a structural disorder occurrence. The lattice morphology was partially reestablished when iodine intercalation was disrupted by its removal at a temperature of about 250°C. The restoring of the rope shape of the SWNT was ascribed to a phenomenon called “zipper-like effect” . Iodine intercalation provoked an up-shift of Raman bands, which may have resulted from a transfer of carbon \( p \)-electrons to the intercalant, inducing a contraction of the hexagonal rings along the cylindrical wall of the SWNTs; this transfer was not observed when vapor instead of molten iodine was used. The Raman spectrum of the \( \text{I}_2\text{-SWNT} \) showed a new band at 175 cm\(^{-1} \) which was assigned to \( \text{I}_x^- \). By Z-contrast scanning transmission electron microscopy, the iodine atoms in the form of helical chains were shown to insert into the SWNTs [369].

Zhou et al. [370] undertook an analytical study of iodine-doped multiwalled carbon nanotubes MWNTs (Figure 34C). Iodine doping was made by immersing the MWNT (the graphene walls of the prepared MWNTs consisted of about 15 layers and the inner diameters of the MWNTs ranged from 0.5 to 7.5 nm) into molten iodine in an evacuated quartz tube at a temperature of 140°C for 1 week. The excess iodine was removed by heating the quartz tube containing the doped MWNTs to about 70°C for 5–6 h. Thermogravimetric analysis indicated that desorption of iodine occurred at room temperature and ended at 200°C, and the carbonization began at 530°C. Raman analysis (\( T=300 \ \text{K} \) and 514.5 nm laser excitation) of a freshly prepared \( \text{I}_2\text{-MWNT} \) showed two bands at 170 and 111 cm\(^{-1} \), assigned to \( \text{I}_5^- \) and \( \text{I}_3^- \), respectively. It was concluded that the larger iodine or iodine chains could not fit between the graphene sheets of the MWNT. Contrary to \( \text{I}_2\text{-SWNTs} \) (\( \text{IC}_{200} \)), the average composition for fresh \( \text{I}_2\text{-MWNTs} \) was found to be close to \( \text{IC}_{200} \) (one iodine atom for 200 carbon atoms).

Bendiab et al. [371] intercalated iodine in SWNT bundles as in [369]. From the weight measurement, the approximate composition was also found to be \( \text{IC}_x \), as reported by Zhou et al. [370]. The \( \text{I}_2\text{-SWNTs} \) were reported to be air stable for months. As evidenced by Raman, X-ray diffraction, and neutron diffraction analyses, iodine doping produced significant changes in the structural arrangement of the SWNT bundles. The iodide species were \( \text{I}_x^- \) (mainly \( \text{I}_1^- \) and \( \text{I}_3^- \) ) and were mostly located inside the tubes. Also, the iodine atoms were not organized in an ordered array with respect to the carbon frame.

Later, Michel and his co-workers [372] confirmed via extended X-ray absorption fine structure (EXAFS) analysis that the iodine-carbon host interaction is weaker in multiwalled carbon nanotubes MWNTs than in single-walled carbon nanotubes SWNTs; the iodine species were localized at the surface of the external tube for MWNTs, but were inside SWNTs. Thermogravimetric analysis was another experimental evidence that showed different energies in the removal of iodine from \( \text{I}_2\text{-MWNTs} \) and \( \text{I}_2\text{-SWNTs} \); indeed, the loss of iodine started at room temperature for the former and only at 100°C for the latter. The iodine in \( \text{I}_2\text{-SWNTs} \) was present mostly as arrays of \( \text{I}_x^- \).

With the aim of enhancing the electrical conductivity (\( \sigma \)) of SWNT, Sankapal et al. [373] designed an iodine-doped nanocomposite made of SWNT-poly(p-phenylene ethynylene)-polycarbonate. It was proven that the electrical conductivity of this iodine-doped nanocomposite was two to five times larger than that of the undoped nanocomposite. For example, \( \sigma \) of the iodine-doped nanocomposite containing 5 wt% of SWNT was 6.86 S·cm\(^{-1} \), compared to 2.56 S·cm\(^{-1} \) for the undoped one. The iodine doping dramatically reduced the insulating polymer gap width. In fact, the insulating polymer barriers of 1 and 5 wt% (SWNT) nanocomposites dropped from 205 to 136 K and from 122 to 5 K, respectively, upon doping.
Recently, Zhao and his group [374] were interested in raising the electrical conductivity of double-walled carbon nanotubes DWNT by iodine doping. The authors preferred the name DWNT cables for these nanomaterials as they may substitute the metallic wires. Iodine doping was conducted by placing the raw DWNT cables (diameter was in the range of 2–3 nm) in the iodine vapor (0.2 mol/l) at 200°C for 12 h. No changes in surface morphology and in diameter were observed upon doping. The results suggested that the iodine was likely to insert inside the shells, but remained mostly on the surface as uniformly distributed clusters (I⁻ and I⁻). XPS analysis of the doped cable (2.3% of iodine) revealed a peak at 285.2 eV, attributed to a C-I bond. The electrical resistivity of I₂-DWNT was in the order of 10⁻⁷ Ω·m and its highest specific conductivity (1.96×10⁴ S·m²/kg) was higher than those of Al and Cu.

An interesting nanocomposite is the nanopeapod, where molecular arrays of C₆₀ fullerenes are encapsulated in SWNTs to form unidimensional nanostructure [375]. Guan et al. [375] examined the assisting effect of doping iodine on the coalescence of C₆₀ molecules inside the SWNTs walls. The procedure was to immerse the C₆₀ peapods in molten iodine in an evacuated glass tube at temperatures of I₂-NP(OMEE) and I₂-[NP(OPr)]n complexes were found to increase with increasing iodine content, and that of I₂-[NPC12]n was slightly higher than that of the undoped polymer. However, a strong endothermic peak was detected for [NP(OTFE)]n at 310 K, which corresponds to the melting of a crystalline phase, and the melting point rose with increasing iodine content. The addition of iodine to ~[-NP(OMEE)]n and ~[-NP(OPr)]n enhanced markedly the electrical conductivities (~10⁻⁴ S·cm⁻¹) of the undoped polymers, whereas almost no effect was observed for the other polyphosphazenes (~10⁻⁵ S·cm⁻¹). The authors suggested that the conduction process involved the polyiodides rather than the polyphosphazene backbones.

Organometallic polymers, namely ferrocene-based ones, have received some attention as far as iodine doping was concerned. Espada et al. [377] and Pannell et al. [378] prepared poly(ferrocenylenesilylene)s and poly(ferrocenylenegermylene)s (Figure 36) by thermal ring-opening of the appropriate ferrocenophane, and treated their thin films (0.1–0.2 μm thickness) with iodine vapor. The pale yellow color of the films turned dark upon iodine doping and the electrical conductivities were measured to be between 2.0×10⁻⁶ and 6.0×10⁻⁵ S·cm⁻¹ for I₂-poly(ferrocenylenesilylene) and poly(ferrocenylenegermylene) (those of undoped polymers were higher than 10⁻¹⁴ S·cm⁻¹). It is of interest that the initial materials recovered by vacuum processing almost retained their conducting property (~10⁻⁷ S·cm⁻¹). The optical spectra gave evidence of a band at 380 nm, a characteristic band of I₃⁺ species, suggesting an

2.2.4 Miscellaneous iodine-polymer complexes

Lerner et al. [376], at a leading school on synthesis and chemistry of polyphosphazenes (Figure 35), iodinated several of them by allowing molecular iodine to diffuse as the vapor into a solid polyphosphazene sample in airtight glass cell at 60°C for several days, until neither solid nor gaseous I₂ remained and the complexes were homogeneous in appearance. The I₂[NPC12]n materials were deep purple and rubbery complexes, whereas I₂-NP(OMEE) and I₂-[NP(OPr)]n complexes were brown-black and tacky liquids, and the I₂-[NP(OTFE)]n complexes were brown and fibrous with morphologies similar to that of the virgin polymer. Raman spectra of the different I₂-polyphosphazenes, with the exception of I₂-[NPC12]n, showed two peaks at 109–113 cm⁻¹ and 164–178 cm⁻¹, assigned to the symmetric stretching mode of I⁻ species and higher polyiodides, respectively; a peak at 145 cm⁻¹ was attributed to the asymmetric stretching mode of I⁻ species. None of these bands appeared in the spectrum of I₂-[NPC12]n because I₂ volatilized from the polymer and recrystallized. The glass transition temperatures of I₂-NP(OMEE) and I₂-[NP(OPr)]n complexes were measured to be between 2.0×10⁻⁶ and 6.0×10⁻⁵ S·cm⁻¹ for I₂-poly(ferrocenylenesilylene) and 3.0×10⁻⁶ and 2.0×10⁻⁵ S·cm⁻¹ for I₂-poly(ferrocenylenegermylene) (those of undoped polymers were higher than 10⁻¹⁴ S·cm⁻¹). It is of interest that the initial materials recovered by vacuum processing almost retained their conducting property (~10⁻⁷ S·cm⁻¹). The optical spectra gave evidence of a band at 380 nm, a characteristic band of I₃⁺ species, suggesting an

![Figure 35](image_url) Polyphosphazenes.

![Figure 36](image_url) Poly(ferrocenylenesilylene)s and poly(ferrocenylenegermylene)s with molecular weights of ~10⁵–10⁶ and MWD of ~1.3–1.8.
oxidation of the polymer giving rise to ferrocenium ions, for which $I_3^-$ is the counteranion. Yet, $^{57}$Fe Mössbauer analysis revealed the existence of the two forms of iron Fe(II) and Fe(III) in approximately equal amounts. In addition, two bands at $-106$ cm$^{-1}$ and another at $-170$ cm$^{-1}$ were seen in their Raman spectra, attributed to $I_1^-$ and $I_2^-$ ions, respectively. The concentration of $I_1^-$ ion increased with greater levels of doping, which was in tune with the observed red shift of the UV absorption and the increasing conductivity of the thin films. $I_2^-$ poly(ferrocenylenesilylene) with R$_2=$MePh was found to contain 1.5 iodine atoms per unit and its glass transition temperature was determined to be $-50^\circ$C, a temperature lower than that for the pristine polymer ($-90^\circ$C), proving the higher rigidity of the complex conferred by links between ferrocenium units and iodide ions [378].

Ramani and Raganathaiah [379] doped polycarbonate (Figure 37A) ($M=28,000$; 26% crystallinity) by soaking the sample in aqueous $I_2/KI$ solution for different intervals of time. The diffusion of the molecular iodine and its sorption on the free volume of the polymer was monitored by PALS. The measured size of the free volume cavities indicated that $I_1^-$ was the most predominant species that filled the cavities. It was found that during the initial stages of sorption, the iodine molecules seemed to diffuse into the free volume cavities in the amorphous regions. Also, it was reasoned that the carbonyl group attached to the main chain in PC could donate electrons to the iodine molecules acting as acceptor dopant, hence CTC formation. The latter CTC formation will provide conducting pathways through the amorphous regions of the polymer and result in the enhancement of the conductivity. The iodine species, having accepted the electrons, become negative charge centers and hence become the attractive sites for positrons. Besides, the diffusion of iodine into PC was congruent with Fick’s law and the variation of the diffusion coefficient with fractional free volume followed Fujita’s predictions.

Ramani and his group [380] extended their work on iodine doping of polymer to poly(ethylene terephthalate) (PET). The latter material, with a molecular weight of 20,000, was soaked in an aqueous $I_2/KI$ solution. By means of the PALS technique, the free volume holes were found to be filled by iodine molecules during the initial stages of sorption, and the most predominant iodine species was $I_1^-$. The PALS results also indicated that the carbonyl groups of the PET were the active sites for CTC formation. During the doping, a conformational change of PET from the coiled to stretched state occurred. Unlike the case of polycarbonate, the diffusion of iodine in PET was found to be of the non-Fickian type, and the variation of fractional free volume with diffusion coefficient did not follow Fujita’s concept of free volume.

Lachinov and Zolotukhin [381] doped thin films of polyaryldiphenylenephthalide (Figure 38), a non-conjugated polymer, with vapor iodine. Electrical conductivity was found to increase with iodine concentration in a large spectrum of temperatures. Significant observations of the behavior of iodine-doped polyaryldiphenylenephthalide occurred for a 50 wt% iodine concentration. Its conductivity ($10^{-3}$ S·cm$^{-1}$) approached that of a metal and became independent of temperature, a fact that is unusual for conjugated polymers such as polyacetylene. Such high conductivity was imputed to an alteration of the electronic structure of the polymer upon doping, leading to a facile delocalization of $\pi$ electrons, and the occurrence of a polaron lattice. As the UV spectrum might have suggested, the doping followed a three-stage mechanism.

Mild carbonization conditions of parylene C [poly(monochloro-p-xylene)] to be used for micro electromechanical systems (MEMS) chips and micro total analysis systems (μ-TAS) applications were conceived by iodine treatment of the polymer [382]. Parylene C was treated with iodine vapor at 90°C (a temperature slightly higher than the $T_g$ of the polymer) for 6 to 12 h. The iodinated parylene C was subjected to pyrolysis at a temperature range of 650–1000°C. The electrical resistivity of parylene C iodinated for 12 h and pyrolyzed at 650°C was 2 $\Omega$·cm and was $3,4\times10^3$ $\Omega$·cm without iodine treatment. In general, its resistivity decreased with increasing pyrolysis temperature. Iodine promoted the carbonization of the polymer at temperatures <700°C. The mechanism by which iodine induced carbonization of parylene C is depicted in Figure 39.

In situ iodine-doped polyterpenol thin films were made by plasma polymerization of terpinen-4-ol.
monomer [383] under an rf power of 25 W. High carbon contents were estimated, up to 76% for pristine film, and up to 84% in the case of iodine doped films. High levels of doping increased the refractive index of the thin films, from 1.54 to 1.70 at 500 nm wavelength, and largely reduced the transparency of films, due to the strong absorption of light by the iodine species. The iodination reduced the bandgap energy in the Tauc relation from 2.82 to 1.5 eV. Also, FTIR and XPS analyses of pristine and iodine doped polyterpenol films revealed a substantial change in the chemical structure of polyterpenol upon iodination; FTIR spectra suggested the formation of a C-I bond. Iodine doped films were more hydrophilic compared to pristine polyterpenol films, as the values of contact angle indicated.

Iodinated polythiophene was conceived by plasma polymerization of thiophene in the presence of vapors of molecular iodine, under an input power of 5 W and a frequency of 13.56 MHz [384]. The material was designed as a chemical sensor. The XPS spectrum of the deposited film showed three peaks at 620.5 eV, 618.7 eV, and 622.4 eV, assigned to molecular iodine, polyiodides I$_3^-$ /I$_5^-$, and oxygenated species of iodine, respectively. According to FTIR and XPS analyses, a chemical structure was proposed for the thus-formed material (Figure 40). Based on resistance measurements, the iodinated plasma-made polythiophene was sensitive to polar and volatile chemicals, such as ethanol, methanol, acetone, ethyl acetate, and ammonia.

Groenewoud et al. [385] prepared polythiophene by pulsed plasma polymerization of thiophene at high pressure (0.3 mBar) and low pressure (0.06 mBar). The obtained polythiophenes were doped with iodine with exposure to iodine vapors at room temperature. A carboniodine bonding occurred as evidenced by FTIR analysis of the iodinated films, stemming from a radical reaction between the polymer and iodine molecule, and the reaction of evolved HI with acetylenic function formed in situ. A maximum conductivity for low pressure polythiophene (≈10$^{-5.5}$ S·cm$^{-1}$) was gained after an exposure time of 40 min, and that for high pressure one (≈10$^{-4}$ S·cm$^{-1}$) after only 5 min. This difference in behavior was explained in terms of difference in the conjugation length. In any case, the conduction mechanism was believed to occur via a hopping transport. Another difference was that the conductivity of the iodine-doped low pressure polythiophene was layer thickness-dependent, that is, it decreased with increasing thickness, and that of the high pressure analogue was not. From the XPS results, the high pressure polythiophene formed more CTCs with iodine than the low pressure counterpart. Also, it was found that the presence of iodine within the polythiophenes reduced the rate of air oxidation.
Wochnowski and Metev [386] carried out polymerization of 2-iodothiophene and 2,5-diodothiophene monomers, mixed with aqueous hydriodic acid under UV-laser irradiation. During the irradiation of the former monomer, a silver-colored thin film was observed on the surface of the liquid phase. The latter phase changed color from yellow to red upon irradiation, hinting at a CTC formation between iodine and the thiophene ring. According to

\[
\begin{align*}
  & 2 \text{HI} \xrightleftharpoons[\text{hv}=248 \text{ nm}]{\text{I}_2 + \text{H}_2} \\
  & \text{I}_2 + \text{S} \xrightarrow[\text{hv}=248 \text{ nm}]{\text{H}} \text{H} + \text{I}_\text{S} \\
  & \text{I}^+ + \text{I}_2 \rightarrow \text{I}_3^- + \text{I}_5^- \quad \text{(polyyiodides as intrinsic doping agents)} \\
  & \text{S} \xrightarrow[\text{I}_5^- + 2\text{I}_5^-]{\text{intrinsic doping}} \text{S} \quad \text{(charge transfer complex)}
\end{align*}
\]

Scheme 15 Mechanism of the polymerization of 2-iodothiophene: (A) generation of iodine molecules in aqueous hydroiodic solution by UV-laser irradiation, (B) formation of charge transfer exciton, (C) formation of polyyiodides as intrinsic doping agents, (D) coupling reaction and formation of a charge transfer complex (CTC), (E) polymerization via dehydrogenation/deiodination and coupling of the radical cationic thiophene oligomers. Reprinted with permission from the corresponding author of Ref. [386].

Abbett et al. [387] conducted iodine doping of poly(3-undecyldithiophene) and its composites with a porous crosslinked polystyrene, using supercritical carbon dioxide (313 K, 10.5 MPa). The latter medium favored a higher iodine level (21.4 wt%) in the composite, and only within 1 h; the ambient conditions (298 K, 0.1 MPa) led to only 9.3 wt% and within 6 days. The conductivity of the I\text{I}_2-composite was 1.2\times10^{-4} \text{ S-cm}^{-1} under the former conditions, and 1.1\times10^{-5} \text{ S-cm}^{-1} under ambient ones. The conductivity of iodinated poly(3-undecyldithiophene) under ambient conditions was measured to be 1 \text{ S-cm}^{-1}, eight orders of magnitude greater than that of non-treated polymer (10^{-6} \text{ S-cm}^{-1}).

A composite polymer made of 5,10,15,20-tetrathienylporphyrin and polythiophene as a novel photoactive thin film (∼200 nm) was prepared by one-step electrochemical polymerization [388]. Iodine doping was done by dipping the composite polymer into acetonitrile solution of iodine for 5 min. Two peaks of binding energies in the XPS spectrum of the iodinated composite polymer were identified at 620.75 eV and 632.35 eV, corresponding to iodine. Such iodine doping level enhanced the photoconversion FTIR and XPS characterizations of the thin film (∼1 μm), an iodine-doped polythiophene and CTCs with polyiodides I\text{I}_3^-/I\text{I}_5^-, were obtained. The mechanism shown in Scheme 15 was thereafter proposed.
efficiency of the solar cell of the film, that is, an incident photon-to-electron conversion efficiency of 32% at 440 nm and a total energy conversion efficiency of 0.12% under 2.59 mWcm² of light intensity. It was proposed that the iodine doping caused a negative shift of highest occupied molecular orbital (HOMO) level of polythiophene, which improved the performance.

Thin films of poly(4,4-dioctylcyclopentadithiophene) (Figure 41A) with a molecular weight of 45,000 were treated with vapor iodine for 15 min in the dark [389]. The blue color of the pristine polymer was lost upon iodine doping, and could be recovered upon the dedoping process. The electrical conductivity of the iodine-doped poly(4,4-dioctylcyclopentadithiophene) was measured to be 0.35 S·cm⁻¹; that of the neutral polymer was only 3.6×10⁻⁶ S·cm⁻¹.

A polymer made by polymerization of alkylthiophenes substituted with a 2-[(4-octylphenylimino)methyl]phenol group, a liquid crystal monomer, via dehydrogenation-condensation using FeCl₃ as oxidizing agent, was doped with iodine vapor for 5 days [390]. The conductivity of the iodine-doped polymer was in the range of 10⁻⁷ S·cm⁻¹, whereas that of undoped one was 10⁻⁹ S·cm⁻¹.

Chen et al. [391] treated poly(isothianaphthene) (Figure 41B), prepared by the method of oxygen-induced polymerization of 1,3-dihydro-isothianaphthene, with iodine in acetonitrile solution of iodine at room temperature for 24 h. Iodine doping was also conducted in the vapor phase under the same conditions. In solution treatment, the iodine content increased with increasing iodine concentration and reached a plateau at about 13% at higher iodine concentrations. Far-infrared spectrum of the iodinated polymer showed a characteristic peak of I₃⁻ at 134 cm⁻¹ and no peak for I₅⁻. In comparison with iodine-doped polyacetylene, this band appeared at a lower wavenumber in the FIR spectrum, suggesting that the interaction between the dopant and the polymer was stronger in iodine-doped poly(isothianaphthene) than in iodine-doped polyacetylene, resulting in weaker I–I bonds. The triiodide ions disappeared (disappearance of the band 134 cm⁻¹) when the iodine polymer was reduced with hydrazine. Raman analysis revealed that I₃⁻ was the dominant species and the band at 1489 cm⁻¹, assigned to a carbon carbon double bond stretching mode of the polymer backbone, shifted to a higher frequency, 1515 cm⁻¹, with increased doping, as with polypyrrole and polythiophene films. Such analysis implied the formation of polaron and bipolaron states in the iodine-doped poly(isothianaphthene).

Silicone, polydimethylsiloxane (PDMS) (Figure 41C), a rubber-like polymer, has been employed in drug delivery systems. Soaking silicone in a saturated ethanolic solution with molecular iodine overnight caused a deep chocolate brown color change [392]. Such iodinated silicone exhibited good antibacterial properties.

Osada and Takase [393] conducted the plasma polymerization of hexamethylocyclotrisiloxane on cellulose acetate substrate, in the presence of molecular iodine. The permeability of the I₂-PHMS membrane towards water was larger than that of the non-doped membrane. However, the permeability of the latter membrane towards alcohols increased with increasing their molecular size and their hydrophobicity, whereas that of doped membrane decreased significantly.

Sorption of iodine by slightly crosslinked polyurethane foam [made of 2,6-toluene diisocyanate (TDI) and polyether polyols] was conducted either by exhibiting the foam to iodine vapors at different temperatures (25, 40, and 70°C) or by immersing it into hexane or toluene solutions of iodine for 2 h [394]. Under the former conditions, the color of the foam changed gradually from white to yellow, then to brown, and finally to black; this color transition was faster at higher temperatures. The iodine uptake increased with temperature and time. For a concentration of iodine of 130 wt%, the conductivity (σ) of iodinated polyurethane attained ~5×10⁻⁶ S·cm⁻¹ and was related to iodine concentration (c) by Log σ=−7.98+0.017c^{0.55}. The Raman spectrum of polyurethane with 70 wt% of iodine showed two most prominent peaks, characteristic for the symmetrical I–I stretching vibrations: 109 cm⁻¹ for I₃⁻ and 169 cm⁻¹ for I₅⁻, I₃⁻ being the major species. It was believed that a CTC was formed between iodine and the benzene ring of the 2,6-TDI unit. This complex produced

![Figure 41](A) Poly(4,4-dioctylcyclopentadithiophene), (B) poly(isothianaphthene), (C) polydimethylsiloxane (PDMS).
physical cross-linking and reduced the mobility of polyurethane chains, which was manifested by an increase in $T_\text{g}$ for an iodine concentration of 110 wt%, $T_\text{g}$ of a material annealed at -15°C for 24 h increased from -46°C to -22.5°C. Under immersion conditions, iodine sorption was higher in hexane (-55 wt% for an immersing time of 30 min) than in toluene (-15 wt%), and in general, it was lower than in vapor process. For biological activity tests purposes, Luo et al. [395] iodinated polyurethane by immersing a polymer film into $\text{I}_2$/$\text{KI}$ aqueous solution at room temperature. The colorless polyurethane film turned yellow and gradually dark purple on prolonging the immersion time; the color did not disappear by repeated washing, suggesting strong $\text{I}_2$ bonding; apparently, a CTC came about between iodine and the benzene ring of polyurethane. The iodine content increased with iodine solution concentration and time. XPS analysis confirmed the iodine binding as CTC via the appearance of two new peaks at 618.8 and 630.0 eV. UV-visible spectrum showed a broad band centered at 350 nm, assigned to $\text{I}_3^-$ ions. The $\text{I}_2$-polyurethane complex demonstrated potent antimicrobial activity against Gram-negative and Gram-positive bacteria, including multi-drug resistant species, fungi, and viruses; they also inactivated bacterial spores and inhibited the formation of bacterial biofilms. Shelanski and his group [396] patented their results on the iodination of TDI-based polyurethane foams and films by different methods, including the immersion of them into an aqueous-alcoholic iodine solution and exposure to iodine vapors for 20–30 min at 58°C; the work was undertaken in view of making an antiseptic detergent. A thermoplastic polyurethane with a molecular weight of 35,000–50,000 was iodinated via the dipping method, for use in medical appliances by virtue of its claimed antibacterial activity [397]. Indeed, iodine-doped polyurethane was conceived as an inactivating substance of the human immunodeficiency virus (HIV), for example, against HIV-I 3B within 15–30 min [398].

A CTC was thought to be responsible for the enhancement of electrical conductivity of iodinated poly(vinylidene fluoride) film (PVF$_2$) [399]. The new band at 270 nm in the UV spectrum was attributed to a CTC formation. Experiments revealed that molecular iodine would have diffused in the amorphous regions of the polymer. In another report [400], iodine doping of polyvinyl butyral (PVB) films not only enhanced its conductivity and reduced the activation energy of the charge carriers, but also modified the nature of the current-voltage $I$-$V$ curves, especially at high fields and high iodine concentrations where the curves tended to become ohmic rather than being non-ohmic.

Electrical conductivities of some non-conjugated polymers (Figure 42) made of short aromatic blocks and methylene chains (benzene, thiophene, and 1,3,4-oxadiazole) changed upon doping with iodine vapor for 10 days [401]. The conductivities increased from $3.6\times10^{-12}$ to $6.9\times10^{-10}$ S·cm$^{-1}$ for non-doped polymers to $6.8\times10^{-8}$ to $9.8\times10^{-5}$ S·cm$^{-1}$ for doped ones; the longer the methylene groups chain, the greater the conductivity. The color of polyoxadiazole polymers changed upon doping from yellow to black and their UV spectra revealed a new band at 370 nm, a characteristic peak of the $\text{I}_3^-$ species. Also, new bands at 1655 cm$^{-1}$, 1505 cm$^{-1}$ and 705 cm$^{-1}$ appeared in the infrared spectra. However, doping poly(p-phenylene-1,3,4-oxadiazole) did not take place, even though it is highly conjugated.

Kumari et al. [402] prepared poly (vinylmercaptobenzothiazole) (PVMBT) from its monomer (Figure 43) and doped it with vapor iodine. The chloroform solution of the iodine-doped PVMBT was orange. The new band in its FTIR spectrum at 1654 cm$^{-1}$, attributed to $\text{C}=$N=– stretching, splitting into two bands at higher iodine concentrations, and a new one at 1590 cm$^{-1}$ also emerged. It was believed that these bands were due to different anions of CTCs. The UV-visible spectrum showed two bands at 511 and 364 nm, assigned to molecular iodine and $\text{I}_3^-$ species. Molecular iodine and PVMBT did not show signals in ESR analysis, whereas an ESR signal of the doped polymer was observed at a $g$ value of 2.0055, indicating the generation of a radical cation within the polymer during doping, due to electron transfer to iodine. The unpaired electron is located more probably on the nitrogen atom of the polymer.

The thermal transition of PVMBT at 55°C increased to 70°C upon doping, suggesting an anti-plasticization effect related to the bonding of chain segments by the dopant. The electrical conductivity of the undoped

Figure 42 Polyoxadiazoles.
PVMBT was measured to be $1.53 \times 10^{-15}$ S·cm$^{-1}$ and tremendously increased to $2.322 \times 10^{-5}$ S·cm$^{-1}$ on doping with 50% of molecular iodine. The conduction process may follow an interchain hopping mechanism.

Bahri and Sood [403] studied the surface photoconductivity of iodine-doped PVC thin films ($\sim 1500$ Å) as function of iodine content. Initially, the photoconductivity increased with increasing concentration of iodine up to a PVC/iodine ratio of 3:3.5, which was ascribed to the CTC formation. Beyond this concentration of iodine, there was a continuous decrease in the photoconduction, which was attributed to a reduced mobility of charge carriers owing to space charge.

Iodine doping was found to affect the stabilization of hetero- and homo-charges in poly(methyl methacrylate) (PMMA) [404], a property that has some industrial applications. This property was estimated by open circuit thermally stimulated current (TSC) and surface charge decay measurements.

### 3 Conclusion

From this review, it appears that the molecular iodine plays a weighty role in polymer science. Polymer responsiveness to molecular iodine treatment undoubtedly manifests, generally in a positive way. An unprecedented finding is the responsiveness of the non-conjugated polymeric hydrocarbons to such a treatment by an unexpected electrical conductivity. It can also be noted the contribution of iodine-polymer complexes to the biological field, as far as antibacterial activity is desired. Polymer complexes induced by iodine molecules are usually colored and the color is generally specific to every polymer. The mechanism of complexation is tightly to the type of organic functions present within the polymer and to its morphology. In many instances, a CT mechanism prevails involving polyiodide ions. In some cases, iodine treatment aids to the transformation of polymers, such the graphitization of PVA and helical polyacetylene. In the light of the outcomes of iodine treatment of polymers, many other phenomena would be unraveled.

Received September 18, 2012; accepted April 17, 2013; previously published online June 11, 2013

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