Interaction Between Iodine and Ethyl Cellulose

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ABSTRACT: Interaction between iodine and ethyl cellulose was investigated by immersing ethyl cellulose membranes in aqueous iodine–iodide solution (iodine doping) and incorporating iodine in the solution from which the membrane was cast. Oxygen and nitrogen permeabilities in iodine-doped ethyl cellulose decrease with an increase in the concentration of iodine in the dopant solution up to 0.003 mol L^{-1} and increase sharply at higher iodine concentrations, and ultraviolet–visible and far-infrared spectra indicate formation of a charge transfer complex. Differential scanning calorimetry of both types of membrane shows changes in the characteristic phase transitions of ethyl cellulose after iodine treatment, including the crystal–liquid crystal transition that has been reported to occur in ethyl cellulose. Further evidence for liquid crystal phases has been found from circular dichroism. X-ray photoelectron spectroscopy of iodine-doped ethyl cellulose films indicates that the iodine is present in two different chemical states, probably I_3^- and I_2. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1303–1314, 1999

Key words: ethyl cellulose; charge transfer complex; iodine doping

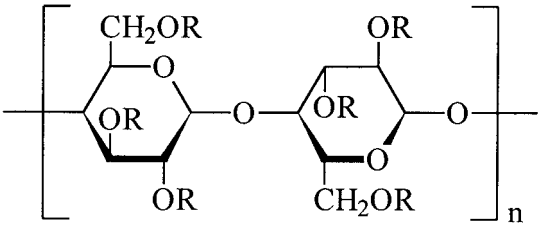
INTRODUCTION

Iodine complexes of polymers are important for many reasons.[1] The doping of polyacetylene films by iodine has been widely studied,[2–5] and yields good electrical conductors. Nylon 6–iodine[1,6] complexes and poly(vinylpyridine)–iodine complexes can be used as electrode materials in lithium–iodide batteries.

The physicochemical effects of iodine on a number of polymers have been investigated in some detail. It has been reported that iodine sorption produces a significant structure change in polymers such as poly(vinyl alcohol),[7,8] poly(acrylonitrile)[9] (PAN), and nylon 6.[1,6] The observed diffraction pattern suggests that iodine penetrates into the crystalline phase of PAN and becomes arranged regularly with PAN chains.[8] Pseudohexagonal crystals of PAN are expanded uniaxially by replacement of PAN molecular cylinders by the polyiodine columns. In iodinated nylon 6, iodine ions form sheets intercalated between sheets of nylon 6 chains to form a paracrystalline lattice.[1] In the case of polyvinyl octal and iodine complex formation, it was found that iodine induces polymeric chain widening and changes the order in the molecular lattice.[10]

The cellulose derivative, ethyl cellulose (EC), has been extensively studied, but there are very few reports on the interaction or complex formation of EC and iodine. Khare and Chardok[11] have studied the films formed on aluminium by dipping an aluminium plate in a solution of EC + iodine and found that the conductivity increases with iodine content of the film.

The EC structure is as follows:



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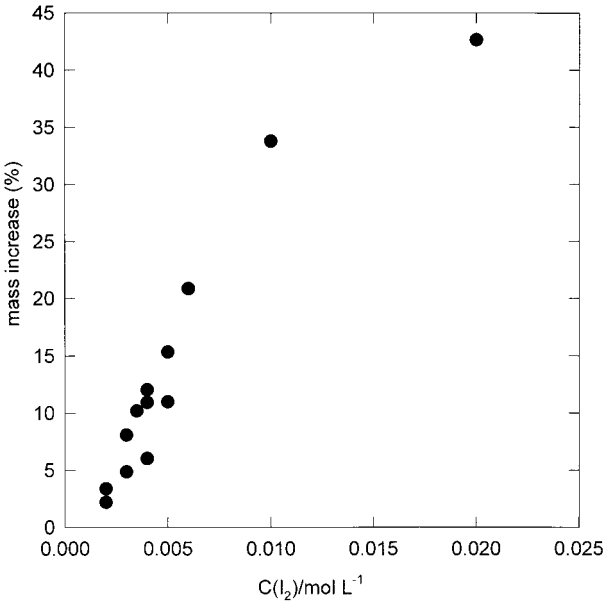


Figure 1 Effect of iodine concentration in the dopant solution on EC membrane weight gain after doping with iodine.

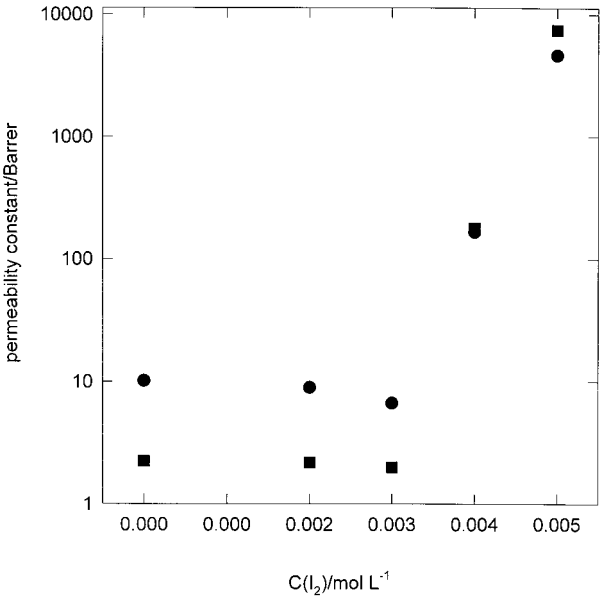


Figure 2 Effect of iodine dopant solution concentration on oxygen and nitrogen permeability at 20°C: (●) oxygen; (■) nitrogen.

The addition of iodine to EC is likely to form charge transfer complexes (CTC) by donor–acceptor interaction between the ether oxygens of ethyl cellulose and iodine molecules. In addition, EC forms both lyotropic and thermotropic liquid crystals under certain conditions due to the rigidity of its anhydroglucose backbone,[8] and it was anticipated that the mesogenic properties can be affected by iodine doping.

In the present work, gas permeability measurements have been used to probe structural changes of EC membranes after iodine doping and following iodine incorporation from the solution from which membranes were cast. The iodine–EC membranes have been further characterized by means of ultraviolet–visible (UV–vis), infrared (IR), and far-IR, and X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), and circular dichroism (CD).

Table I Oxygen and Nitrogen Permeability Constants for Iodine-Doped Ethyl Cellulose

$C(I_2)$/mol L^{-1}	$P(O_2)$	$P(N_2)$
0	10.2	2.24
2×10^{-3}	8.9	2.17
3×10^{-3}	6.7	1.98
4×10^{-3}	166	179
5×10^{-3}	4.66×10^3	7.48×10^3

The permeability constant is expressed in Barrer.

EXPERIMENTAL

Materials

Ethyl cellulose was supplied by Acros Organics (Belgium). The ethoxy content was nominally

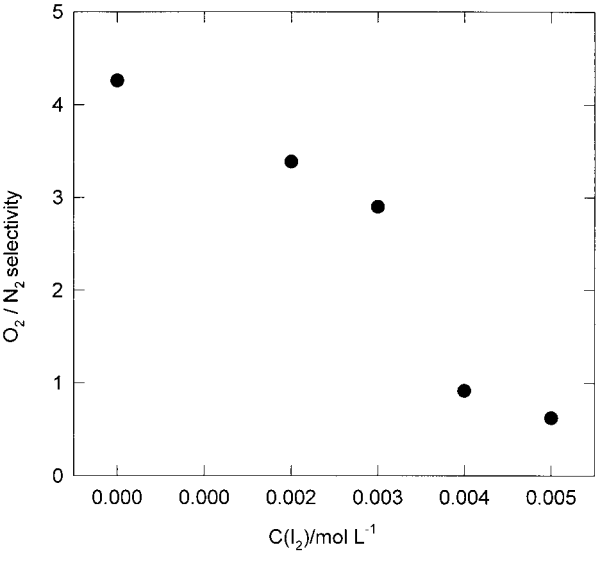


Figure 3 Effect of iodine dopant solution concentration on oxygen to nitrogen selectivity.

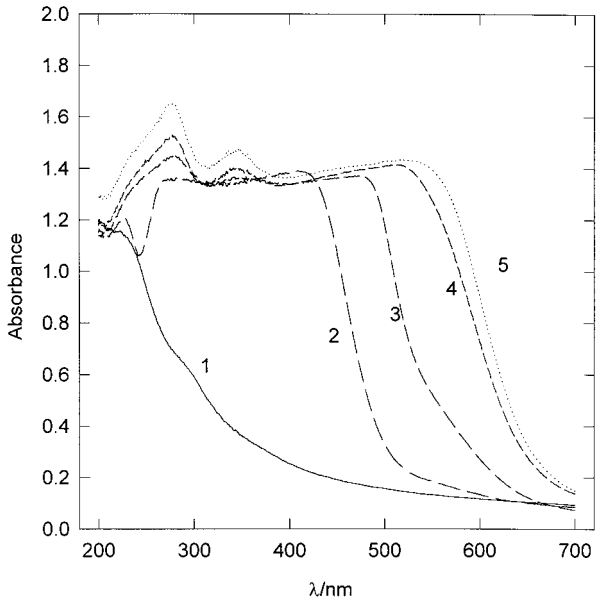


Figure 4 UV spectra of iodine-doped ethyl cellulose: (1) pure EC; (2) 0.002; (3) 0.003; (4) 0.004; (5) 0.005 mol L^{-1} iodine solution.

48%, and the viscosity of a 5% solution in 80/20 toluene to ethanol was nominally 100 mPa s. Iodine and potassium iodide were reagent grade materials. Dichloromethane, chloroform, and tetrahydrofuran were used as received.

Membrane Preparation

Ethyl cellulose films were cast from 3% w/w solution in dichloromethane, chloroform, and tetrahydrfuran (THF) in 13.6-cm-diameter glass petri dishes. The solvent was allowed to evaporate at ambient temperature for 24 h, and the membranes were then dried in vacuum for 24 h to remove residual solvent. The membranes so formed were of the order 50–100 μm thick.

Iodine Doping

Ethyl cellulose films were immersed in aqueous I_2–KI solutions of different concentrations at room temperature for 24 h to attain equilibrium sorption.

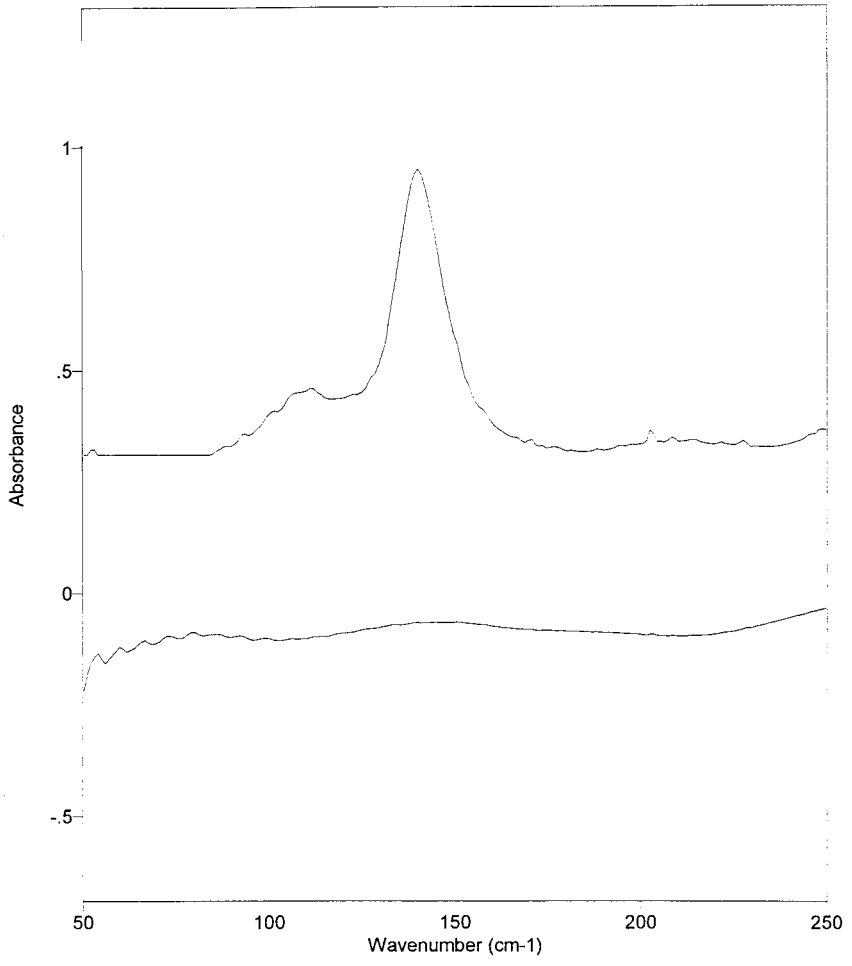


Figure 5 Far-IR spectrum of EC and EC doped in 0.004 mol L^{-1} iodine solution.

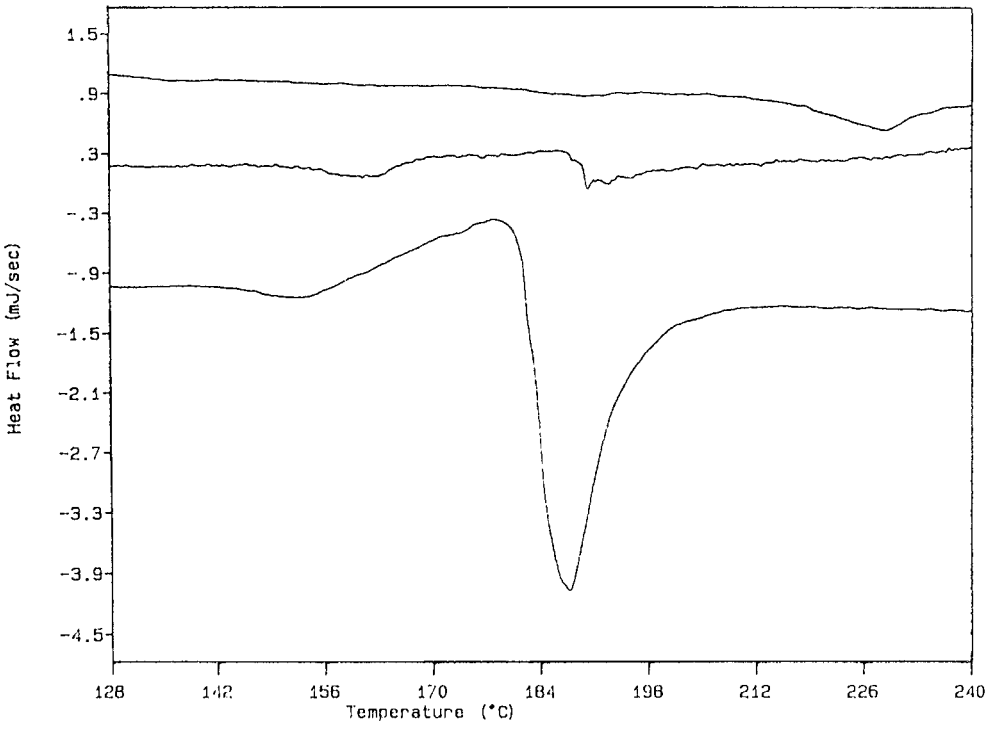


Figure 6 DSC scans of iodine-doped EC films: (upper) undoped EC; (middle) EC doped in 0.002 mol L^{-1} iodine solution; (lower) EC doped in 0.004 mol L^{-1} iodine solution.

The iodinated EC films were rinsed with water and dried between sheets of filter paper in vacuum for 24 h at ambient temperature. The amount of iodine sorption was determined from the increase in weight of a dry film before and after doping.

Iodine Incorporation During Casting

Different amounts of iodine were incorporated in EC casting solutions by dissolution of appropriate amounts of elemental iodine. The resulting membranes were rinsed with water and dried in vacuum as for the iodine-doped membranes.

Characterization

UV–vis spectra of iodine-doped membranes were recorded using a SHIMADZU UV 2101 PC UV–VIS scanning spectrophotometer. Far-IR spectra were recorded on a Digilab FTS-60 Fourier transfer infrared (FTIR) spectrometer. Spectra were obtained in the absorbance mode between 60–500 cm^{-1}, and 64 scans were averaged to give a consistent spectrum at a resolution of 2 cm^{-1}.

Thermal analysis was performed using DSC (Polymer Laboratories Model 12000 instrument) at a heating rate of 10°C min^{-1}, in an atmosphere of dry, oxygen-free nitrogen.

Circular dichroism (CD) spectra of films were determined with a Jasco model 720 instrument in the wavelength range of 200–800 nm.

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos XSAM 800 X-ray photoelectron spectrometer.

Gas permeability constants were determined using equipment designed and constructed in our laboratory. Sample membranes in the form of circular discs 9.0 cm in diameter were mounted in a thermostatted permeation cell operating on the volume-increase principle. The downstream side of the cell was maintained at atmospheric pressure. The pressure on the upstream side was adjusted with a needle valve and read by a pressure sensor of type Sen Sym 618A SCX 100 DN. Steady-state conditions were attained in about 30 min, after flushing both sides of the membrane with test gas for 8–10 min.

RESULTS AND DISCUSSION

Iodine-Doped Ethyl Cellulose Film

When ethyl cellulose membranes were immersed in iodine–potassium iodide solution, iodine was

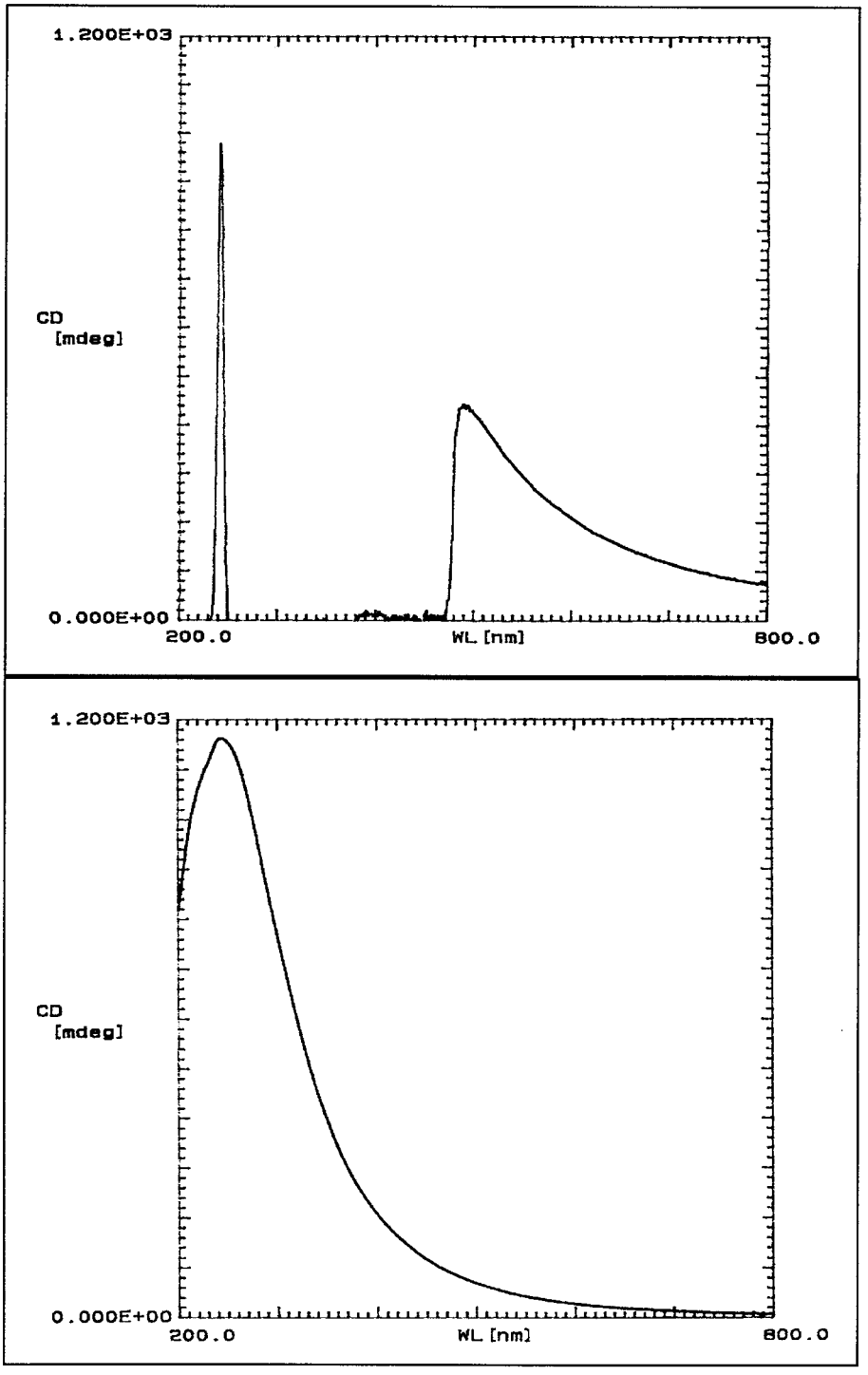


Figure 7 Induced CD spectra for EC (lower) and EC doped in 0.004 mol L^{-1} iodine solution.

readily absorbed into the polymer. The treated membranes developed a characteristic orange to brown color, depending on the iodine concentration. The intensity of the color increased with doping time, suggesting formation of a charge transfer complex, which remains after rinsing and vacuum drying.

Figure 1 shows the amount of iodine absorbed by EC films as a function of the iodine concentration in the doping solution, relative to the initial

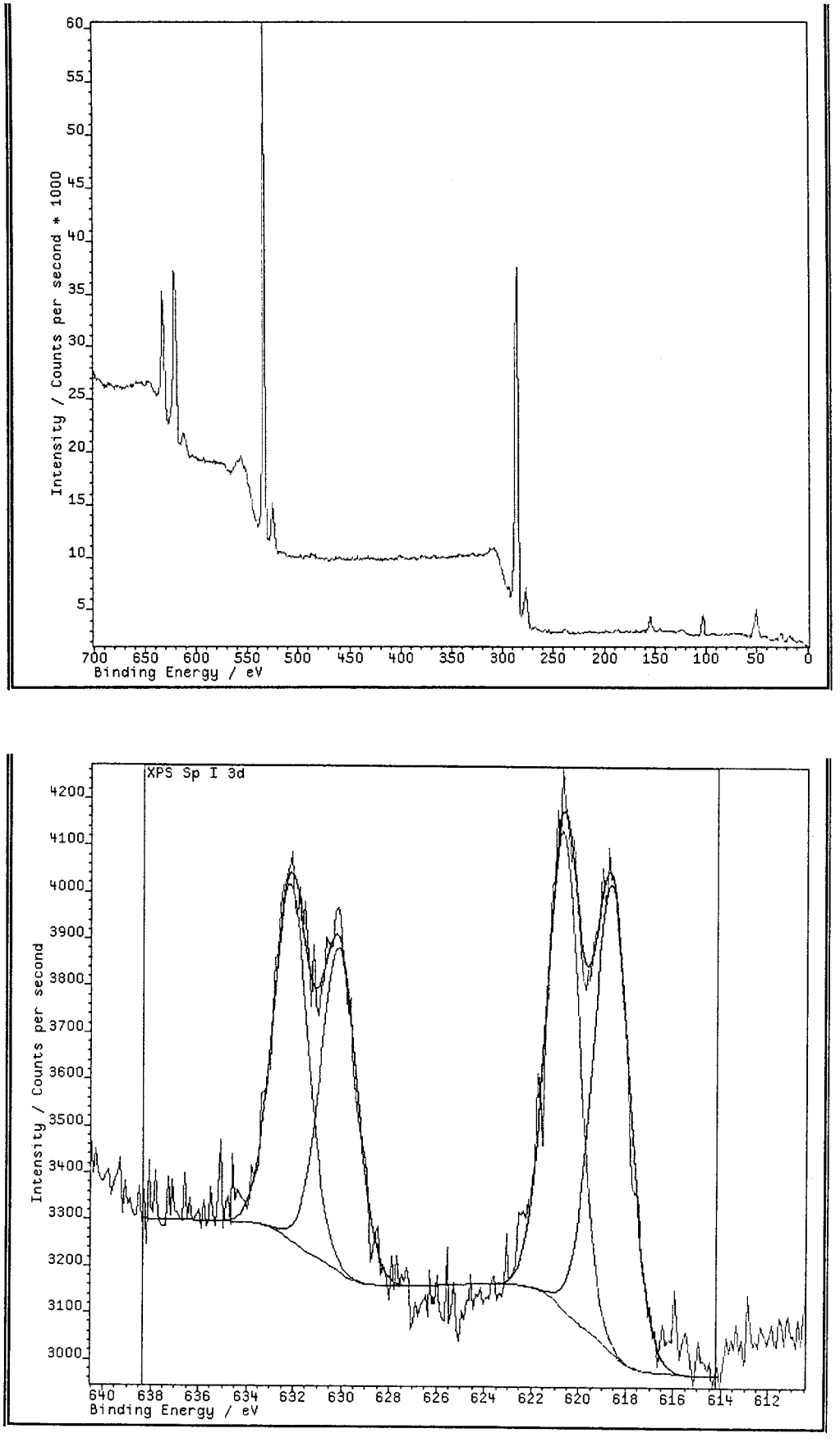


Figure 8 XPS scans of iodine-doped EC film.

weight of the film. Iodine absorption increases rapidly with iodine concentration, at concentrations smaller than about 0.01 mol L^{-1}, and much less rapidly at higher concentrations.

Gas Permeability

Ethyl cellulose has been the subject of research for oxygen enrichment applications since the 1950s. The permeability of a polymer is determined primarily by the magnitude of the free volume, and it was anticipated that incorporation of a significant proportion of large iodine molecules in EC should change the free volume and influence the magnitude of the permeability. In addition, it was expected that the distribution of free volume could be modified, leading to a change in the selectivity of the membrane.

Oxygen and nitrogen permeability constants of the iodine-doped membrane are given in Table I and are shown graphically in Figure 2. Both the oxygen and nitrogen permeabilities initially decrease slightly with the iodine concentration in the dopant solution and, hence, with the amount of iodine absorbed. This trend can be attributed to the formation of charge-transfer complexes that restrict polymer chain mobility and reduce free volume. It is possible that a reduction in the solubility of O_2 and N_2 contributes to lower gas permeabilities, but it is more likely that the principal factor is reduced diffusion coefficients for oxygen and nitrogen.

A striking feature of Figure 2 is the dramatic increase in permeabilities of both gases when the iodine concentration of the dopant solution exceeds 0.003 mol L^{-1}. The increase in permeability is exponential in iodine concentration at concentrations above 0.003 mol L^{-1}. There appears to be a threshold iodine concentration (around 0.003 mol L^{-1}) above which the mechanism of gas transport through the membrane changes such that a more facile route for gas permeation becomes available.

Somewhat similar behavior has been found for polyacrylonitrile. Kim found that high iodine dopant levels cause a striking change in PAN,[9] whose crystalline structure expands. According to the intercalation model,[12] it is possible that at a higher concentration, iodine intercalates between polymer chains in the form of a polyiodine column and opens the polymer structure, allowing gas molecules to diffuse more rapidly.

The gas selectivity is defined as the ratio of gas permeabilities measured under the same conditions. Figure 3 shows the effect of the iodine doping solution concentration on oxygen to nitrogen selectivity. The iodine-doped membrane becomes more permeable to nitrogen than to oxygen when the iodine concentration is higher than 0.003 mol L^{-1}.

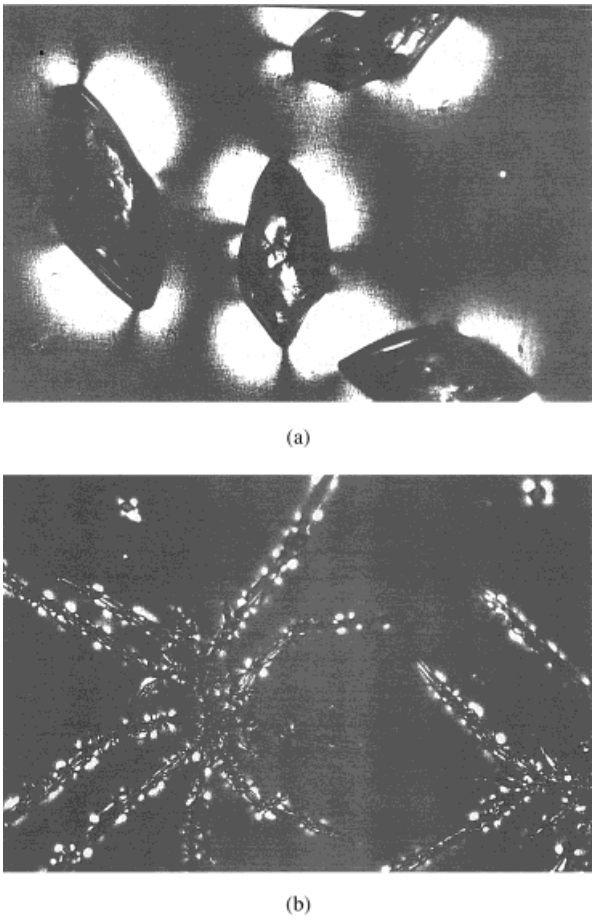
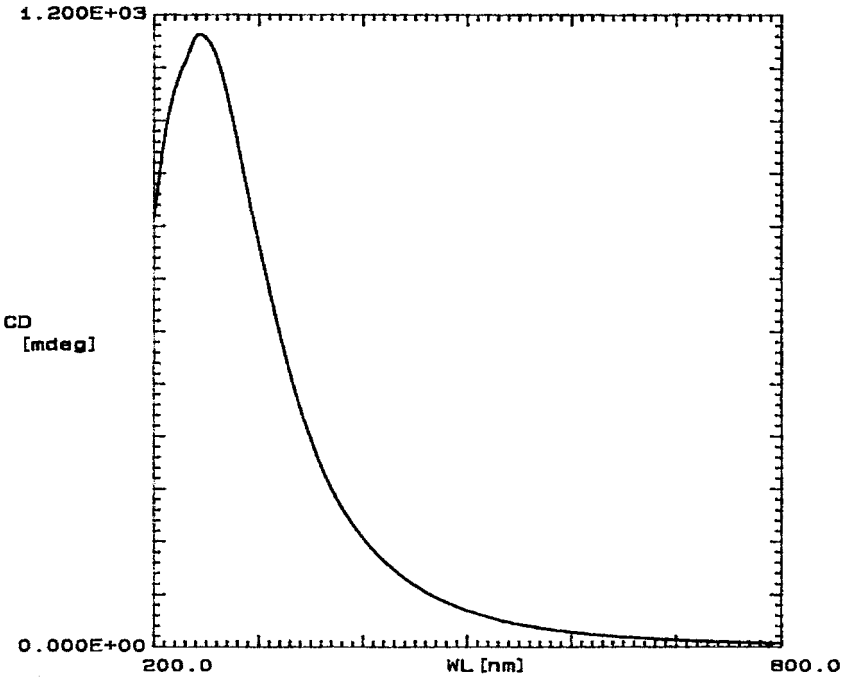


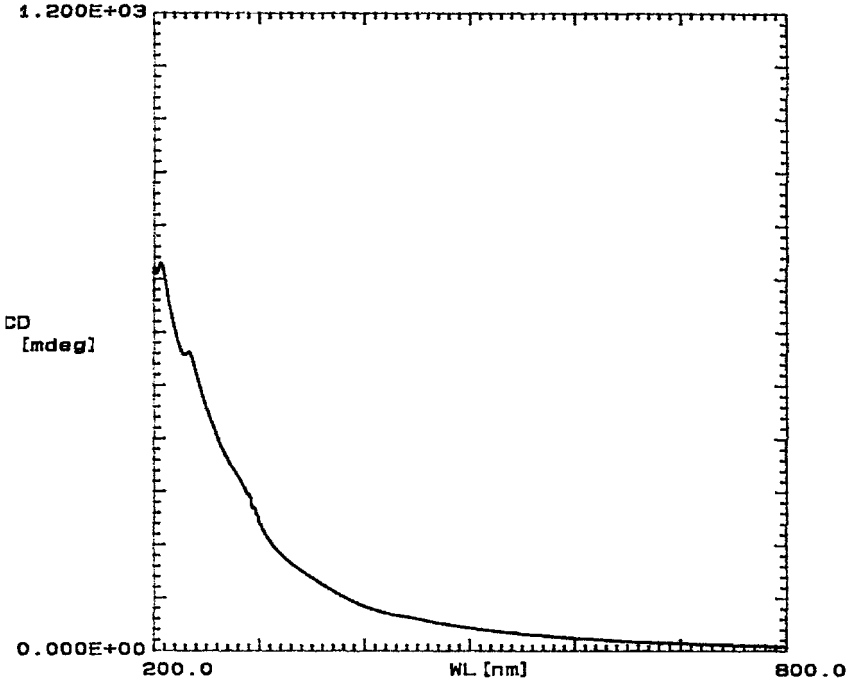
Figure 9 Typical crystalline structures produced by incorporation of iodine in EC during casting from chlorinated alkane solution: (a) single crystals; (b) crystalline microfibers. The magnification is about 200× for (a) and (b).

UV, Far-IR, and DSC Characterization of Iodine-Doped Ethyl Cellulose

Figure 4 shows a series of UV–VIS absorption spectra of the I_2–EC complex formed by EC films immersed in I_2–KI solutions with different iodine concentrations. Ethyl cellulose exhibits no band in the visible region, and the spectrum of iodine-doped ethyl cellulose shows bands that are attributable to a charge transfer complex. The absorption maxima at around 280 and 350 nm increase with increasing iodine concentra-



(a)

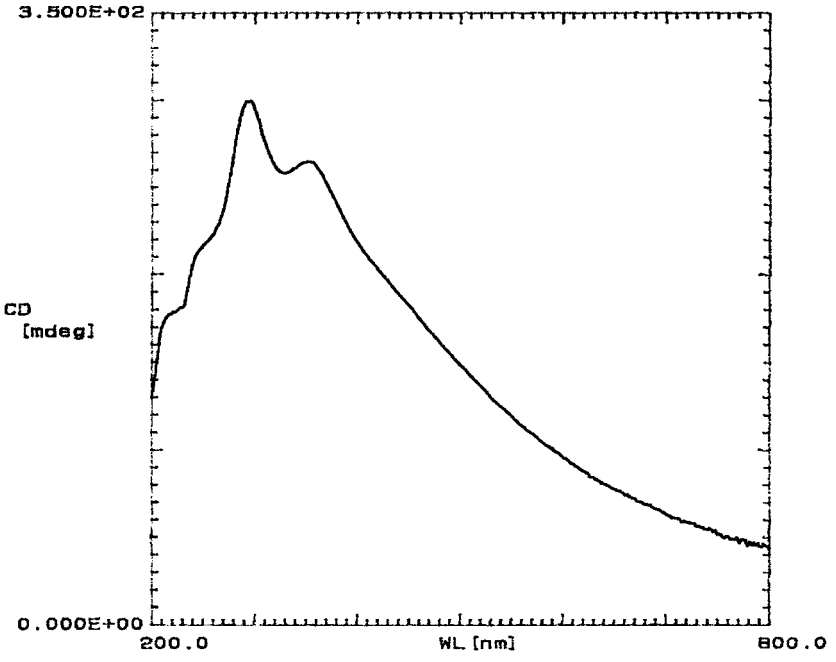


(b)

Figure 10 CD spectra of EC films with iodine incorporated during casting: (a) pure EC; (b) 40% iodine, cast from tetrahydrofuran; (c) 40% iodine, cast from dichloromethane.

tion. The 280 and 350 nm bands arise from the CT complex with I_2–I_3^-[5], and the broad absorption band in the 480–600 nm range is due to unreacted I_2.[9]

The far-IR spectrum of iodine-doped EC (Fig. 5) show a strong absorption at 138 cm^{-1}, assigned to the complex[13,14] EC–I_3^-. No absorption at 180 cm^{-1} (expected for I–I stretch) appears.



(c)

Figure 10 (*Continued from the previous page*)

DSC scans of pure EC films exhibit three phase transitions due to its ability to form a thermotropic liquid crystal. According to Chen and coworkers,[15] the transition at 188°C is a solid–mesophase transition, and that at 228°C is the mesophase–isotropic liquid transition. The other transition at 135°C is the glass transition. After iodine doping, it was found that the endotherm at 228°C became hard to detect, while a sharp endotherm appears at 183°C (Fig. 6). This could be the result of EC becoming more crystalline due to CT complex formation and chain ordering, and to iodine sublimation, since the iodine sublimation temperature is 180°C. The endotherm at 183°C vanished from a second DSC scan on the same sample, suggesting that the endotherm is associated with iodine sublimation.

CD Spectra

EC film cast at room temperature from solution is an orientationally ordered glass, where the chiral nematic structure, initially present in the liquid crystalline solution, is retained on drying.[16] Figure 7 shows CD spectra for the films. The EC film (lower spectrum) exhibited a positive peak at each wavelength, that is, the cotton effect, indicating that the cast film retained left-handed cholesteric liquid crystalline order. The wavelength of the peak is directly proportional to the pitch.[17] Iodine-doped EC film (upper spectrum) shows two CD bands. The first arises from EC cholesteric order and occurs near 250 nm, and the second, near 490 nm, may be assigned to CD induced in iodine.

Iodine-doped EC film exhibits induced optical activity due to association of iodine via a strong oriented interaction with chiral centers on the cellulose chain. Evidently, iodine also adopts the cholesteric helicoidal arrangement. Induced optical activity has previous been observed[18] for the dye Congo red bound to regenerated cellulose.

Chemical State of Iodine

The nature of the iodine species in iodine-doped polymers depends on the polymer. It may be an ionic (I_3^-, I_5^-, I_7^-, polyiodide) or neutral (I_4, I_6) species.[19] X-ray photoelectron spectroscopy has been used to determine doping levels and the nature of doping species. In Figure 8 (upper spectrum), a wide scan of iodine doped EC shows strong iodine absorption. The iodine $3d_{3/2}$–$3d_{5/2}$ core level narrow scan spectrum is shown in the lower spectrum. The splitting is indicative of two types of iodine. The iodine $3d_{5/2}$ levels can be deconvoluted

into two components, at 618.8 and 619.9 eV, possibly attributable to I_2 and I_3^-.[20,21]

Based on the experimental observations, it is suggested that the interaction between iodine and ethyl cellulose proceeds as follows:

1. iodine sorption;
2. iodine molecules forming a charge transfer complex with ether oxygen of ethyl cellulose;
3. iodine changing from an achiral to a chiral form;
4. iodine penetration into the liquid crystalline phase of EC, changing the structure of the parent polymer.

Ethyl Cellulose with Iodine Incorporated During Casting

Murthy and co-workers reported[2] that immersing polyacetylene in an aqueous KI–I_2 solution produces polyacetylene–iodine complexes, which are very similar to those obtained both by vapor-phase doping, and by doping with iodine dissolved in organic solvents, such as heptane and pentane.

To better understand the behavior of iodine-doped ethyl cellulose membrane, iodine was incorporated into ethyl cellulose solution before casting. Iodine is retained by the resulting EC film, giving orange–brown membranes.

When the proportion of iodine in the casting solution is greater than 40% (w/w) of the EC content, the films cast from solution change from being homogeneous and amorphous, into partially crystalline, multiphase structures. Optical microscopy shows iodine-induced crystallinity appearing as either single crystals [Fig. 9(a)] or crystalline microfibres [Fig. 9(b)] imbedded in an amorphous matrix. The single crystals formed were not recrystallized iodine; they were colorless and had a sharp melting point (determined with a microscope with heating stage) of 230°C, very close to that of pure EC. It seems that when iodine is incorporated in the casting solution, the strong interaction that leads to CTC formation decreases side chain mobility, changes the EC conformation, and brings about alignment of the highly flexible and mobile chains, thus facilitating crystallization. A complicating factor is that the single crystals produced by casting from an EC–iodine solution (in chloroform, for example) gave no X-ray reflections, suggesting some form of molecular disorder. That the single crystals are not chemically different from the matrix EC was confirmed by IR microscopy. Reflectance spectra of the single crystals were not discernibly different from spectra of the adjacent matrix.

EC membrane with iodine incorporated during casting has different CD spectra (Fig. 10) from iodine-doped membranes. The intensity decreases as the amount of incorporated iodine increases, and the spectrum shows a fine structure. In contrast to iodine-doped EC, no discrete band at 490 nm appears.

DSC scans of EC and two membranes with different proportions of iodine present in the casting solution are shown in Figure 11. The glass transition temperature is reduced only slightly by incorporation of iodine, but both the crystal → mesophase and mesophase → isotropic liquid transition temperatures are substantially reduced. Furthermore, for the membrane cast from a solution with 40% iodine, there is a marked change in the shape of the melting endotherm. The associated phase transition appears to occur in two stages, a gradual first stage that leads to a very sharp endotherm in the second stage.

The solvent influences the interaction between iodine and ethyl cellulose. No crystalline phase appears at even higher amounts of iodine incorporated into EC–THF solution, and no cotton effect was observed for the membranes cast from THF solution. The solvent effect can be explained by the fact that formation of charge transfer complexes between the two components is strongly enhanced in polar chlorohydrocarbons[22] because the hydrogen atom from the chlorohydrocarbon enhances the electrophilic nature of I_4 and I_2.

Using XPS, a very weak iodine peak was detected in films made by incorporating high levels of iodine in EC at the casting stage. The doping level is determined from the integrated intensity of the peaks. Table II gives the elemental analysis from XPS for I, C, and O for iodine-doped EC films and chemical microanalytical data for C, H, and O for films with iodine incorporated during casting. It appears that iodine is lost by evaporation from films with iodine incorporated during casting. The implication is that the EC-iodine interaction is stronger, and the iodine less labile in the iodine-doped membranes.

CONCLUSIONS

Iodine, when doped in polymers, may reside at various sites.[23] It may go substitutionally into the polymer chain or reside at the amorphous–crystalline boundaries and diffuse preferentially through the amorphous regions and form charge

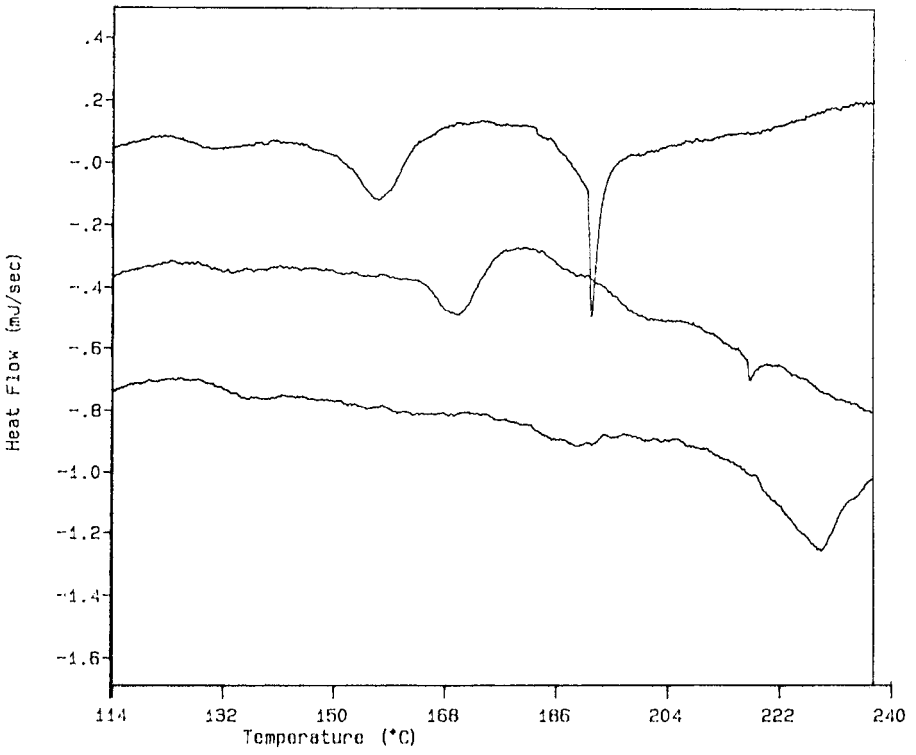


Figure 11 DSC scans of pure EC (lower trace), EC with 20% (middle), and EC with 40% (upper) iodine in the casting solution.

transfer complexes (CTC), or it may exist in the form of molecular aggregates.

In case of ethyl cellulose, it is quite likely that molecular iodine may be diffusing in the amorphous phases of the polymer and forming CTC with the polymer chains. The formation of CTC is usually characterized by the appearance of a new charge-transfer absorption band in the absorption spectrum of the doped polymer, and that is the case for iodine-doped EC. Moreover, iodination of ethyl cellulose films produces a significant change in the structural order of EC, while iodine-doped EC film exhibits induced optical activity due to association of iodine with chiral centres on the cellulose chain.

In the case of iodine incorporated during casting, the EC structure is affected by iodine and solvent. At a high level of iodine in the casting solution, apparently, crystalline structures are formed. It seems that the strong interaction between EC and iodine facilitates ordering of EC molecules, allowing nucleation and crystal growth to occur as the solvent evaporates.

Table II Elemental Analysis (Wt %) of Iodine-Doped EC and EC with Iodine Incorporated During Casting

Membrane	C	H	O	I
EC[a]	56.9	8.9	34.2	—
EC (I_2-doped)[b]	50.2	(7.9)	30.2	11.8
EC (I_2 incorporated, 20%)[c]	55.2	8.8	(35.4)	0.6_5
EC (I_2 incorporated, 40%)[d]	55.4	8.8	(34.9)	0.9_0

The parenthesized figures were obtained by the difference.
[a] Calculated.
[b] From XPS, assuming that relative proportions of C, H, and O are unchanged.
[c] From microanalysis (20% iodine in casting solution).
[d] From microanalysis (40% iodine in casting solution).

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