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Electrical and Optical Properties of a Novel Nonconjugated Conductive Polymer, Polynorbornene

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We report electrical and optical properties of a novel nonconjugated conductive polymer, polynorbornene which has an isolated double bond in the repeat. Electrical conductivity of this polymer increases by twelve orders of magnitude to about 0.01 S/cm upon doping with iodine. Optical absorption measurements of the polymer film have been made at different dopant concentrations. For a lightly doped polymer, two absorption peaks: one corresponding to cation radicals and the other corresponding to charge transfer between the double bond and the dopant were observed at 4.20 eV (295 nm) and 3.13 eV (396 nm) respectively. FTIR spectroscopic measurements have shown reduction in the intensities of the C=C stretching and =C-H bending vibration bands upon doping indicating formation of radical cations. Photoluminescence studies have shown an emission band with a major peak at ~422 nm when excited at 280 nm. The peaks in the photoluminescence spectrum are consistent with the vibration bands observed in the FTIR spectrum.

Keywords: Nonconjugated conductive polymers, polynorbornene, electrical and optical properties, photoluminescence, FTIR

1 Introduction

Organic molecular and polymeric electronic materials are important to study in view of a wide range of applications in electronics and photonics (1–8). Nonconjugated conductive polymers were first reported (9) by Thakur in 1988. Since then, significant attention has been paid to nonconjugated conducting polymers and various applications have been demonstrated (10, 11). The electrical conductivities of nonconjugated conductive polymers such as polyisoprene, poly(alloocimene) and poly(β -pinene) increases by more than ten orders of magnitude upon doping with electron acceptors such as iodine (12–14). Recently, iodine-doped nonconjugated conductive polymers have been shown to have exceptionally large nonlinear optical properties. Unexpectedly high quadratic electro-optic effects have been observed in nonconjugated conducting polymers including doped cis-poly(isoprene) and poly(β -pinene) (12, 15). The Kerr coefficient of poly(β -pinene) measured at 633nm was reported to be $1.2 \times 10^{-10} \text{ m/V}^2$. This value is fifty times greater than that of nitrobenzene. An exceptionally large two-photon absorption coefficient, α_2 of $\sim 2.6 \text{ cm/MW}$ at 1.53 eV was observed for doped poly(β -pinene) (16). Such high optical nonlinearities of nonconjugated polymers have been attributed to the nano-metallic domains formed, when

these polymers are doped with iodine. Due to their high optical nonlinearities, these polymers have wide variety of applications in photonics. In this report, electrical and optical properties of a novel nonconjugated conducting polymer polynorbornene (18, 19) are discussed. The molecular structure of polynorbornene is shown in Figure 1.

2 Experimental

2.1 Electrical Conductivity

As shown previously, the maximum conductivity of a nonconjugated conducting polymer depends on the number fraction of its double bonds per repeat unit. The maximum conductivity of polyisoprene which has a double-bond number fraction of $1/4$, is 0.1 S/cm. Poly(alloocimene), which has a double bond number fraction of $1/3$ reaches a maximum conductivity of 1S/cm, while poly(β -pinene) with double bond number fraction of $1/6$, has a maximum electrical conductivity of 0.008 S/cm. In this report, we discuss electrical conductivity of polynorbornene which has a double-bond number fraction of $1/5$. For this polymer, we expect a maximum conductivity between those of polyisoprene and poly(β -pinene). Table 1 shows the maximum electrical conductivities and the corresponding double bond number fractions of specific conducting polymers

Polynorbornene samples obtained from Aldrich (average Mw > 2,000,000) were powdered and dissolved in benzene.

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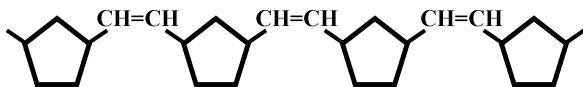


Fig. 1. Molecular structure of polynorbornene.

The polymer solution was then used to cast a thin film on a glass slide. Initial weight of the polymer and the conductivity of the film were measured. The film was then doped with iodine; the weight uptake of iodine and the corresponding conductivity of the film were noted at regular intervals. The conductivity of the polymer was observed to increase with increase in dopant concentration. A maximum conductivity of 0.01 S/cm was observed corresponding to an iodine concentration of about 1.0 molar. This value is in between those of poly(β -pinene) and polyisoprene. The conductivity of polynorbornene as a function of molar concentration of dopant is shown in Figure 2. A comparison of the conductivities of some of these nonconjugated conducting polymers are shown in Table 1.

It should be noted that the double bond number fraction of polynorbornene is 1/5 and its conductivity lies between that of cis-poly(isoprene) and poly(β -pinene) as one might have expected. When the polymer is doped with iodine, cation radicals are formed. The number of cation radicals formed is directly proportional to the molar concentration of iodine. The holes formed when the polymer is doped are responsible for the increased conductivity. Molecular structure of doped polynorbornene with the cation radicals formed due to iodine doping is shown in Figure 3.

2.2 Optical Absorption

The undoped film of polynorbornene is transparent. The film turns brownish green upon doping with iodine. Optical absorption measurements were performed on polynorbornene film at different dopant concentrations using thin films cast on quartz substrates. The spectra are shown in Figure 4. The lightly doped polymer has two peaks at 295 nm (4.20 eV) and 396 nm (3.13 eV). The peak at 4.20 eV corresponds to the cation radicals formed due to doping and the peak at 3.13 eV corresponds to the charge transfer

Table 1. Conductivities of nonconjugated conducting polymers with different double-bond number fractions (Ref. 9–14).

Polymer	Double bond number fraction	Electrical Conductivity (S/cm)
Poly(β -pinene)	1/6	0.008
Polynorbornene	1/5	0.01
Cis-poly(isoprene)	1/4	0.1
Poly(alloocimene)	1/3	1.0
Polyacetylene (Conjugated polymer)	1/2	~100

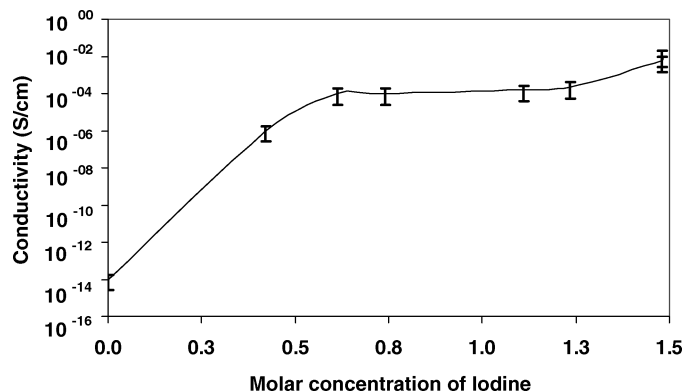


Fig. 2. Electrical conductivity of polynorbornene as a function of molar concentration of iodine.

between the double bond and the dopant. When the dopant concentration is increased, the intensity of the peak at 4.20 eV increases and the peak corresponding to charge-transfer broadens and undergoes a red shift. This behavior is observed in other nonconjugated conducting polymers such as poly(β -pinene) (14) and cis-poly(isoprene) (12).

The optical absorption of doped nonconjugated conducting polymers such as polynorbornene is comparable to that of metallic nanoclusters (15, 16). The absorption peak of a nanocrystal is a function of the particle size. With increase in particle size the absorption peak broadens and red shifts (17). For a nanometer-size silver particle, the absorption peak (17) is at about 425 nm (Figure 5). In doped polynorbornene, the charged state is confined within a sub-nanometer domain and as a result its absorption peak is at about 396 nm. These nano-optical materials are expected to exhibit exceptionally high optical nonlinearities.

2.3 FTIR Spectroscopy

FTIR spectroscopic studies of polynorbornene as a function of dopant concentration (iodine) were performed using a Nicolet 5PC FT-IR spectrometer. KBr pellets of undoped and doped polynorbornene were made and used to obtain the spectra. The spectra were corrected for water absorption. The FTIR studies show a decrease in the peak intensities at 1718 cm^{-1} and 967 cm^{-1} corresponding to C=C stretching and =C-H bending vibration bands respectively, upon doping with iodine (Figure 6 a–d). The C=C transforms into cation radicals upon doping and charge-transfer.

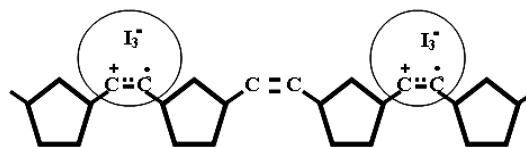


Fig. 3. Molecular structure of doped polynorbornene.

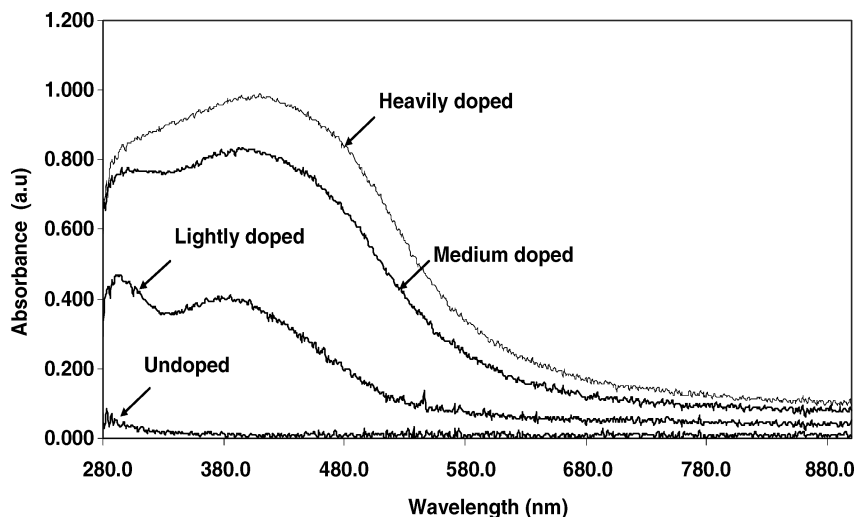


Fig. 4. Optical absorption spectra of polynorbornene.

The decrease in the peaks at 1718 cm^{-1} and 967 cm^{-1} is directly related to the dopant concentration.

2.4 Photoluminescence

Photoluminescence measurements were performed on polynorbornene using a Perkin-Elmer LS-55 spectrometer. The undoped polymer has a weak absorption at about 280 nm. When the undoped polymer was excited at 280 nm photoluminescence spectrum from 350 nm to 500 nm was observed with a major peak at 422 nm along with a number of vibrational bands. The spectrum is shown in Figure 7. The shifts calculated from the wavelengths of these peaks [shift = $(1/\lambda - 1/\lambda')$] compare well with the vibration bands observed in the FTIR spectrum. This is shown

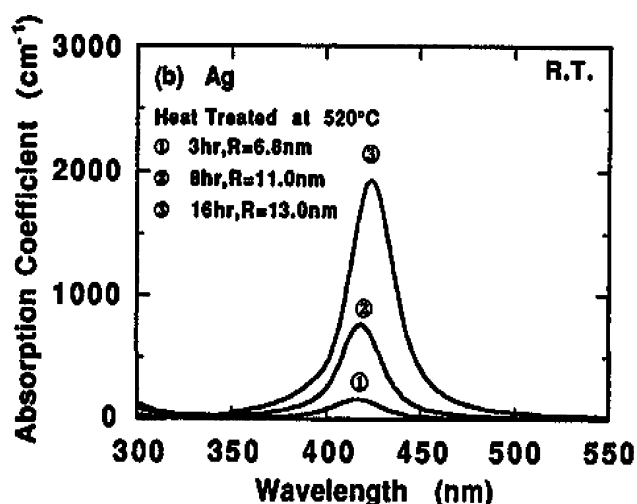


Fig. 5. Optical absorption spectra of silver nanoparticles of different sizes (ref. 17).

in Table 2. The photoluminescence in polynorbornene is quenched upon doping with iodine.

3 Results and Discussion

As reported here, polynorbornene is a novel nonconjugated conductive polymer. Undoped polynorbornene has very low electrical conductivity. When doped with iodine, its electrical conductivity increases by about twelve orders of magnitude. The maximum conductivity of this polymer was found to be 0.01 S/cm . The magnitude of the maximum conductivity is consistent with the double-bond number fraction ($1/5$ per repeat) of this polymer (Table 1). The optical absorption spectrum of the lightly doped polymer has two distinct peaks: one at 4.20 eV corresponding to cation radicals and the other at 3.13 eV corresponding to charge transfer between double bond and dopant. When the dopant concentration is increased, the intensity of the peak due to cation radicals increases and the peak due to charge transfer broadens and undergoes a red shift. FTIR measurements show a decrease in $\text{C}=\text{C}$ when the polymer is doped with iodine. This decrease is because of the charge-transfer from the

Table 2. Vibrational wavenumbers calculated from photoluminescence peaks (Figure 7) using shift = $(1/\lambda - 1/\lambda')$, and compared with peaks in the FTIR spectrum.

Shifts calculated from photoluminescence peaks	Corresponding FTIR Wavenumber	Bond involved
$1 \rightarrow 4$	2950 cm^{-1}	C-H stretching
$2 \rightarrow 3$ and $3 \rightarrow 5$	1718 cm^{-1}	C=C stretching
$5 \rightarrow 6$	967 cm^{-1}	=C-H bending

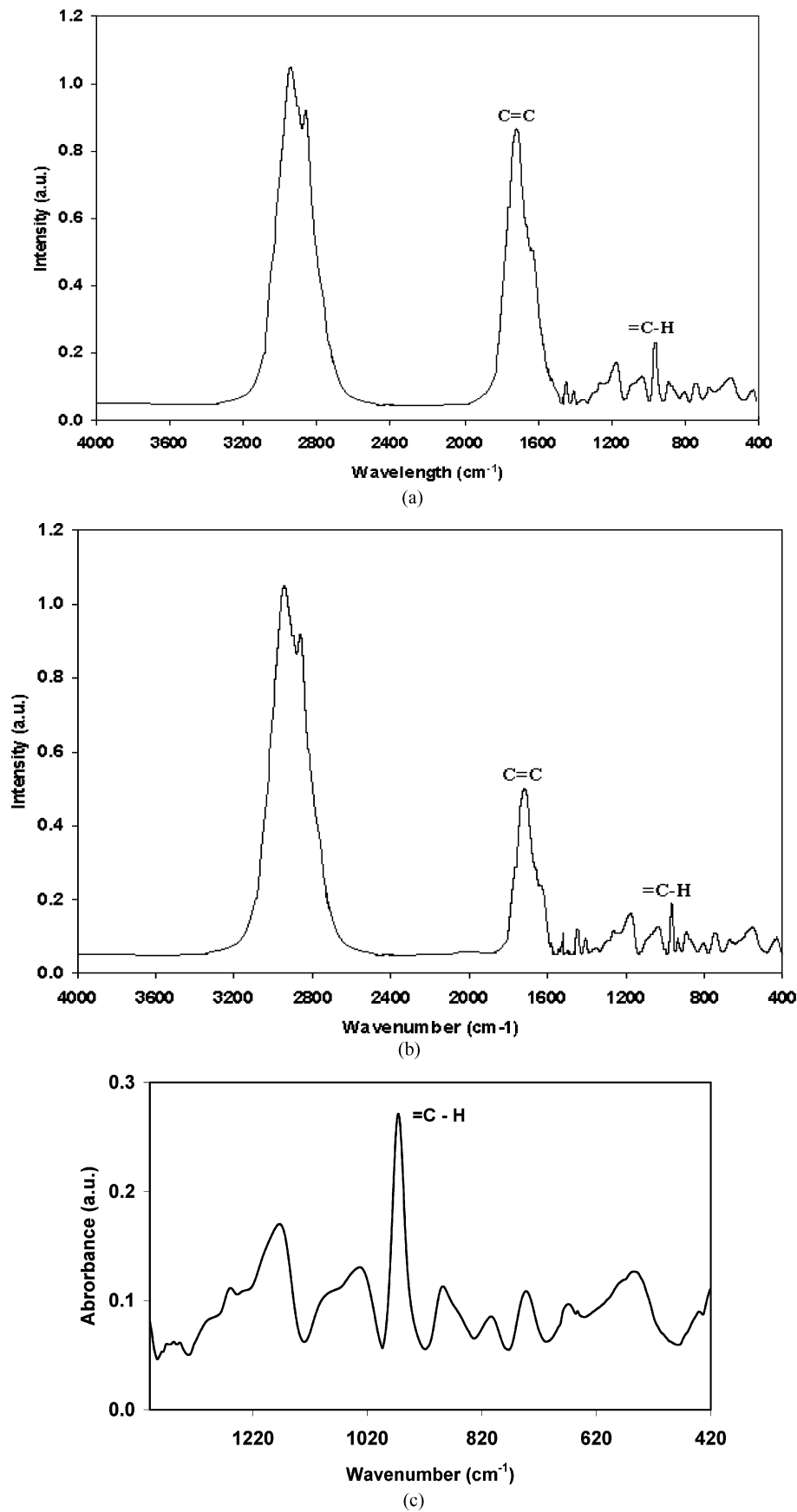


Fig. 6. (a) FTIR spectrum of undoped polynorbornene; (b) FTIR spectrum of doped polynorbornene; (c) FTIR spectrum of undoped polynorbornene at lower wavenumbers; and (d) FTIR spectrum of doped polynorbornene at lower wavenumbers. (*Continued*)

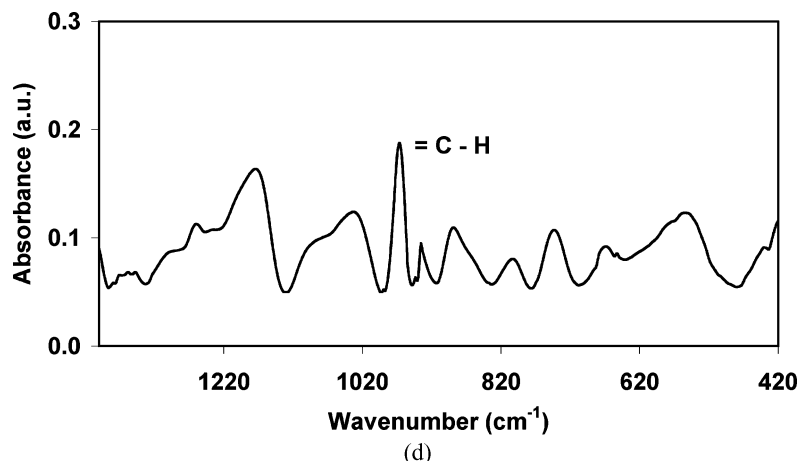


Fig. 6. (Continued)

double-bond to the dopant and formation of radical cations. Photoluminescence measurements show an overall emission peak at 422 nm when the polymer is excited at 280 nm. The other smaller peaks in the photoluminescence spectrum have wavelengths consistent with the vibration bands (Table 2) observed in the FTIR spectrum. Upon doping with iodine the photoluminescence of the polymer is quenched. The charge-transfer state formed upon doping of polynorbornene is confined within a sub-nanometer domain leading to a novel nano-optical polymer which may exhibit high third order optical susceptibility similar to other doped nonconjugated conductive polymers.

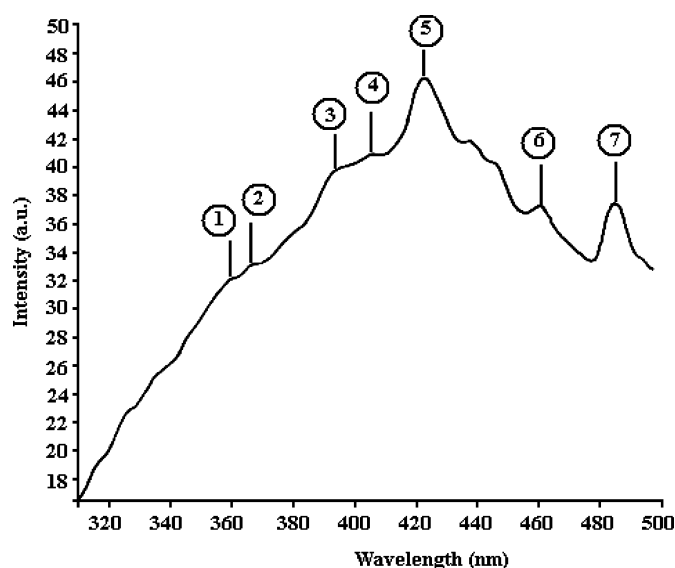


Fig. 7. Photoluminescence spectrum of undoped polynorbornene for excitation at 280 nm.

4 Conclusions

In conclusion, electrical conductivity, optical absorption, FTIR and photoluminescence in a novel nonconjugated conductive polymer, polynorbornene have been measured for different doping levels of iodine. Upon doping, the conductivity increased by about twelve orders of magnitude to about 0.01 S/cm consistent with its double-bond number fraction (1/5) per repeat. For a lightly doped polymer, two absorption peaks: one corresponding to cation radicals and the other corresponding to charge transfer between the double bond and the dopant were observed at 4.20 eV (295 nm) and 3.13 eV (396 nm) respectively. FTIR spectroscopic measurements have shown reduction in the intensities of the C=C stretching and =C-H bending vibration bands upon doping indicating formation of radical cations. Photoluminescence studies have shown an emission band with a major peak at ~422 nm when excited at 280 nm. The peaks in the photoluminescence spectrum are consistent with the vibration bands observed in the FTIR spectrum.

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