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NOTE

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Electrical conductivity, FTIR spectroscopy and electro-optic effect in a novel nonconjugated conductive polymer, poly(β -pinene), have been recently reported. The conductivity increases by more than ten orders of magnitude upon doping with iodine. The double bonds decrease upon doping due to charge-transfer and formation of radical cations. In this report, electron paramagnetic resonance (EPR) spectroscopic measurements of poly(β -pinene) before and after iodine doping are discussed. The results show that the EPR signal increases in proportion to the doping level consistent with the formation of radical cations upon doping. Hyperfine splitting has been observed at high doping levels due to reduction in distance between the radical cation and the iodine anion. Such splitting was not observed for a doped conjugated polymer since in that case the radical is delocalized.

Keywords: radical cation; epr; hyperfine splitting; nonconjugated conductive polymer; poly(β -pinene)

1 Introduction

Electronic and optical polymers have attracted significant research attention because of the fundamentally interesting characteristics and a wide range of potential applications. Nonlinear optical properties of organic and polymeric materials have various applications in photonics. The research on nonconjugated conductive polymers was initiated in 1988 (1), and the field has attracted significant research interest since that time (2–4). Detailed studies of nonconjugated conductive polymers have been made using various spectroscopic methods including optical absorption, FTIR, Raman, ¹³C-NMR, Mossbauer and EPR. Various applications of these polymers have been demonstrated. Nonconjugated conductive polymers such as doped polyisoprene are important materials having confined electronic or nano-optical structures (5). Exceptionally large quadratic electro-optic effect (third order optical susceptibility) has been reported for iodine-doped polyisoprene (5). Electrical conductivity, FTIR spectroscopic and photoluminescence characteristics of a novel nonconjugated conductive polymer, poly

(β -pinene) have been recently reported (6). Large quadratic electro-optic effect in iodine-doped poly(β -pinene) due to formation of nano-optical domains has been recently reported. The molecular structures of poly(β -pinene) before and after doping with iodine are shown in Figure 1(a) and (b), respectively. The doping leads to a charge-transfer from the isolated double bond to iodine forming radical cations. In this report, the results of electron paramagnetic resonance (EPR) measurements of poly(β -pinene) for different doping levels to confirm formation of radicals are discussed.

2 Experimental

The electrical conductivity of poly(β -pinene) increases by more than ten orders of magnitude upon doping with iodine. Undoped poly(β -pinene) has conductivity less than 10^{-12} S/cm. Upon doping with iodine, the conductivity increases rapidly. When the molar concentration of iodine (number of iodine atoms per repeat) reaches about 0.85, the conductivity saturates (6) at $\sim 8 \times 10^{-3}$ S/cm.

Optical absorption and FTIR spectroscopic results of poly(β -pinene) have been reported (6). The optical absorption spectra for different dopant concentrations are shown in Figure 2. Two major optical absorption peaks have been observed for lightly doped samples: one at 4 eV (310 nm)

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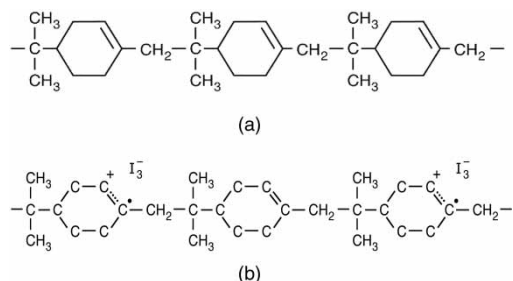


Fig. 1. (a) Molecular structure of undoped poly(β -pinene), (b) Radical cations formed in poly(β -pinene) upon doping and charge-transfer.

corresponding to cation radicals and the other at 3.1 eV (400 nm) due to the charge transfer between the donor and the acceptor. The lower energy peak undergoes a red shift when the dopant concentration increases. This is due to the reduction of the average distance separating the radical cation and the iodine anion (6, 7). FTIR spectra of the polymer before and after doping are shown in Figure 3. Upon doping, there is a decrease in the FTIR peaks at 1610 cm^{-1} and 728 cm^{-1} corresponding to C=C stretching vibration and =C-H bending vibration respectively. This decrease is due to charge-transfer from the isolated double-bond to the dopant and formation of radical cations (Figure 1b). In the present report, we discuss results of EPR measurements to show that cation radicals are formed upon doping of poly(β -pinene).

The EPR measurements were performed on poly(β -pinene) at different doping levels of iodine. The poly(β -pinene) samples used in this work were purchased from Aldrich Chemicals Corp. Films of poly(β -pinene) were prepared on a glass substrate from a toluene solution. The films were then doped with iodine at different concentrations. The

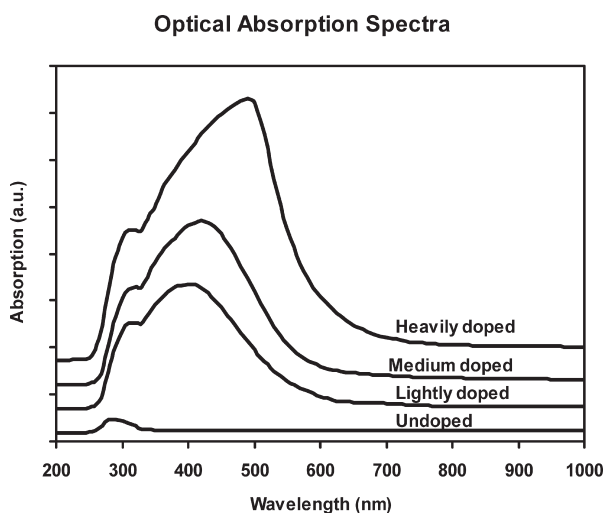


Fig. 2. Optical absorption spectrum of poly(β -pinene) at different dopant concentrations.

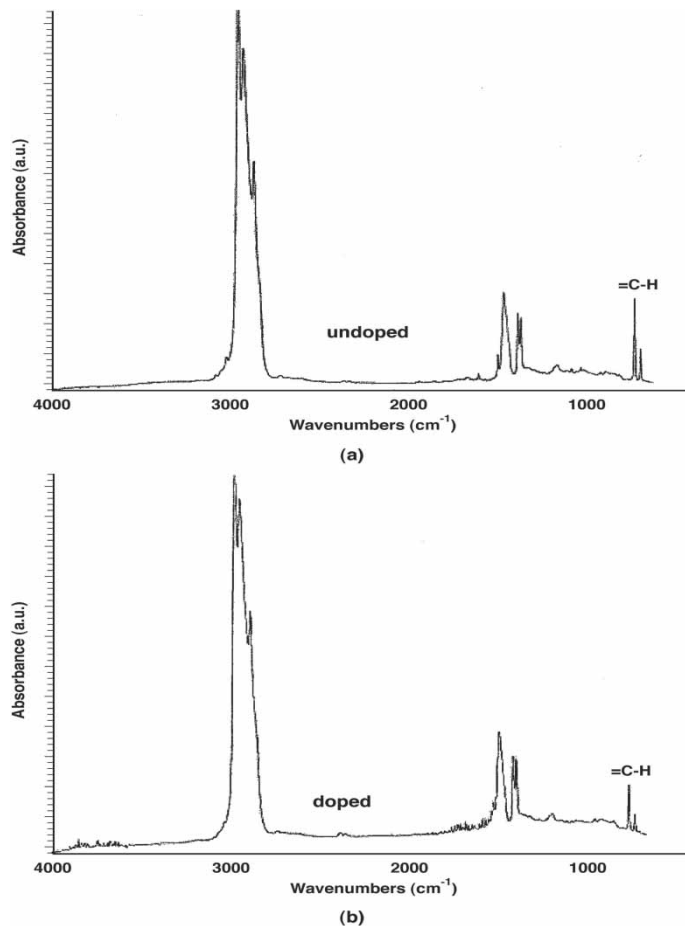


Fig. 3. FTIR spectra of poly(β -pinene): (a) undoped, (b) iodine doped.

molar concentrations were calculated by measuring the weight uptake of iodine in the film. The powder samples obtained from the doped films were used to perform the EPR measurements. Undoped poly(β -pinene) samples were also prepared as a powder and weighed to perform the EPR measurement. The EPR experiment was conducted at X-band (9 GHz) using a Bruker EMX spectrometer at room temperature, as well as at a lower temperature (100°K). Cooling of the sample was performed with an Oxford Instruments ESR 900 flow cryostat with an ITC4 temperature controller.

3 Results and Discussion

The undoped poly(β -pinene) sample showed a very weak EPR signal (Figure 4) due to the methyl radicals (9). Significant EPR signals increasing in proportion to the dopant concentration have been observed and the results are shown in Figure 4. Clearly, the EPR signal of the heavily doped sample is large. As these results have shown, $g = 2.0042$ and the EPR line-width (ΔH_{pp}) of the doped samples is about 13 G. These values compare well with those of doped

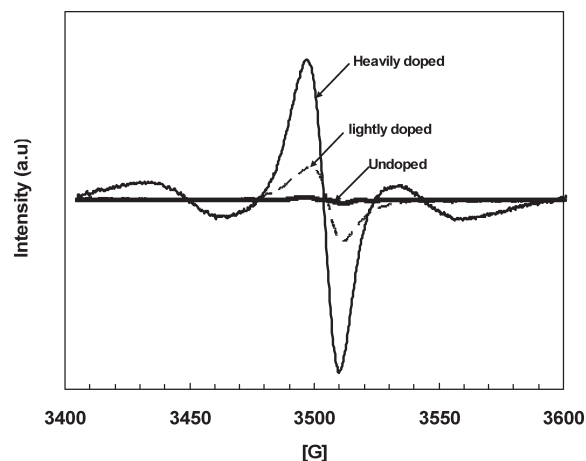


Fig. 4. EPR signals of poly(β -pinene) at different dopant concentrations.

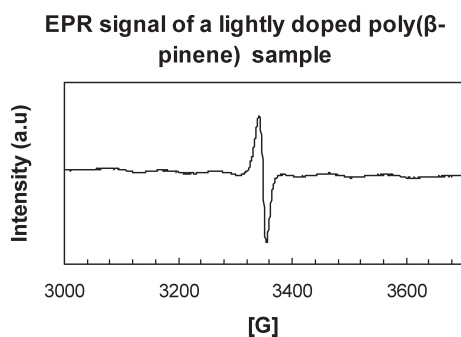


Fig. 5. EPR signal of lightly doped poly(β -pinene).

cis-polyisoprene reported earlier (7). The line-width is larger compared to that in conjugated conductive polymers (8, 10–12) because the radical is less mobile (confined) in the case of the nonconjugated conductive polymer. The EPR signals of a lightly doped and a heavily doped sample are shown in Figures 5 and 6, respectively. Hyperfine splitting was

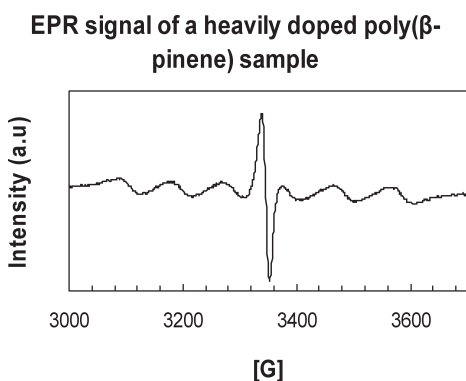


Fig. 6. EPR signal of heavily doped poly(β -pinene).

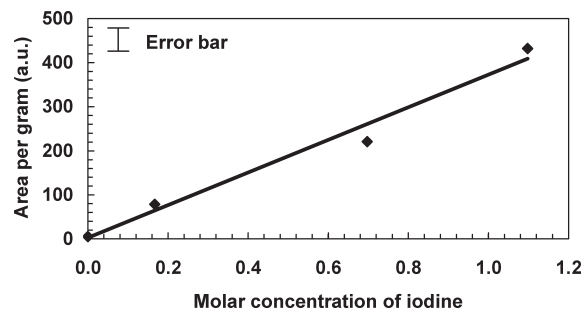


Fig. 7. Area under the curve (double integral of the EPR signal) as a function of molar concentration of iodine showing that the radical concentration is proportional to the doping level.

observed in the EPR signal particularly in the case of heavily doped samples (Figure 6). Six peaks due to hyperfine splitting were observed. If there are 'n' nuclear spin halves, $n+1$ distinct peaks due to hyperfine splitting are expected in the EPR signal. Iodine has a nuclear spin of $5/2$. Therefore, six peaks as a result of hyperfine splitting, can be expected and were observed. At the high dopant concentration, there is a reduction in the distance between the cation radical and the iodine anion leading to the hyperfine splitting as observed. Such splitting has not been observed for a high-doped conjugated polymer since in that case the radical is delocalized keeping a relatively larger distance with the iodine nucleus. Although doping leads to I_3^- as the counterion, (1b) only one iodine atom can get close enough to the radical to cause significant hyperfine splitting as observed. Therefore, only six peaks are observed. This is because of the structural rigidity and the molecular complexity of poly(β -pinene). The hyperfine coupling constant as determined from the data is 479 G. The results indicate that the coupling is fairly isotropic.

The area under the curve determined from the double integral of the EPR signal (at 100°K) was plotted as a function of molar concentration of iodine, and the correlation is shown in Figure 7. The area per gram increases linearly with the molar concentration of iodine. Since the area is proportional to the spin concentration, the results show that the concentration of radicals increases proportionally with the doping level. As stated earlier, these results clearly show that cation radicals are formed upon doping and consequent charge-transfer from the isolated double bonds to the dopants. At higher doping levels, a hyperfine splitting of the EPR signal is observed. These results should be compared with conjugated polymers such as polypyrrole, poly(phenylene vinylene) and others (8, 10–12). In polypyrrole and PPV, the spin concentration initially increases with the dopant concentration due to formation of radical cations (polarons) and then decreases at higher doping levels because of formation of bipolarons. Formation of bipolarons in the case of a nonconjugated conductive polymers is energetically less feasible. In addition, the EPR line-widths in doped conjugated polymers are significantly narrower than that of

nonconjugated conductive polymers due to delocalization in conjugated polymers (8, 10–12).

4 Conclusions

In summary, EPR measurements have been performed on poly(β -pinene) at different concentrations of iodine. The signal was found to increase proportionally with the iodine concentration due to the formation cation radicals upon doping and charge-transfer. The results are consistent with the FTIR and optical absorption data. The g -value and the EPR line-width (ΔH_{pp}) compare well with that of another nonconjugated conductive polymer, doped 1,4-*cis*-polyisoprene (7). Hyperfine splitting in the EPR signal has been observed for heavily doped samples because of reduced distance between the cation radical and the iodine anion. Such splitting has not been observed for a heavily doped conjugated polymer, since in that case, the radical is delocalized keeping a larger distance with the iodine nucleus.

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