



# Electro-optic materials from co-polymeric elastomer–acrylonitrile butadiene rubber (NBR)

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## Abstract

Recently, we demonstrated that conjugated sequences of unsaturated double bonds can be introduced into co-polymers such as styrene butadiene rubber (SBR), which contains isolated double bonds along the polymer backbone through conjugation reactions induced by iodine [Sreeja R. Submitted for publication [1]]. Here, we report for the first time the doping reaction in another notable co-polymer nitrile rubber, a co-polymer of acrylonitrile and butadiene. The conductivity reaches a value of about 0.01 S/cm with the characteristic color change from colorless to dark red upon doping. FT-IR and UV/VIS studies of the polymer film establish the formation of conjugated sequences of the unsaturated double bonds followed by the formation of charge transfer complexes with the dopant ion. The reaction is analogous to the iodine doping of SBR for longer doping period and retained flexibility of the film after doping. However, the band gap evaluated is greater for NBR and this increase can be explained as due to the presence of electron withdrawing –CN groups in place of electron releasing phenyl group in the SBR backbone, which can cause a partial influence on the chemical reaction along the polymer backbone. The excellent oil resistance, abrasion resistance and mechanical properties of NBR combined with the newly developed semi conducting behaviour can be utilized for fabricating various electronic and optical devices based on this elastomer.

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**Keywords:** Acrylonitrile butadiene rubber (NBR); Conjugation; Conductivity

## 1. Introduction

Polymerization of conjugated dienes can frequently lead to the formation of linear polymers containing main chain double bonds. Examples of such diene monomers are buta-1,3-diene; 2-methylbuta-1,3-diene (isoprene); 2,3-dimethylbuta-1,3-diene and 2-chlorobuta-1,3-diene (chloroprene). Polymerization of these materials via the 1,4-position yields polymers with a flexible backbone containing isolated double bonds. These diene rubbers are now significant in another perspective—as conducting elastomers. The discovery in 1988 by Thakur, that the conductivity of *cis*-1,4-polyisoprene (natural rubber) can be increased by 10 orders of magnitude upon doping with iodine [2] generated a great deal of interest in the polymer electronic industry. Since then, various other diene rubbers were also reported to become dark in color and conductive when ‘doped’

with iodine [3–6]. Based on these results, Thakur concluded that a conjugated backbone is not always necessary for a polymer to be electrically conducting. Later, papers published by Dai and co-workers established evidences for the possibility of double bond shift reactions, on iodine doping resulting in the formation of conjugated sequences of unsaturated double bonds in the polymer backbone [7].

Several other elastic materials can be made by co-polymerizing one of the above monomers with lesser amounts of one or more monomers. Notable amongst these are SBR, a co-polymer of butadiene and styrene and nitrile rubber (NBR), a co-polymer of butadiene and acrylonitrile. Since these materials also contain isolated double bonds, the I<sub>2</sub>-doping reactions can be envisaged and we have already reported the transition of SBR into a semiconductor at room temperature [1]. This study reports a similar reaction in NBR and a comparative study with iodine doping in SBR has been done so as to clearly identify the effect of the nature of second component of the co-polymer in the doping reaction. The significant difference between the two co-polymers is that SBR contains electron releasing phenyl group and NBR contains

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electron withdrawing –CN groups along the polymer backbone.

Conjugated polymers have been considered promising materials for opto-electronic applications since the discovery of electroluminescence in poly(*p*-phenylene vinylene) [8,9]. Most semiconducting polymers appear to have a band gap that lies in the range 1.5–3 eV, which makes them ideally suited as opto-electronic device working in the optical light range [10]. Moreover, polymers are also easier to process and fabricate into different shapes. Thin semiconducting layers can be formed by spin or dip coating from a solution of the polymer. They also offer the possibility of coating large areas. Finally, the mechanical properties of polymers (e.g. flexibility, toughness, elasticity, etc.) are unique and can lead to completely new types of devices [11].

Thus this work is aimed at the development and characterization of conducting elastomer from NBR [nitrile rubber, Buna-N, or acrylonitrile butadiene rubber], which is a complex family of unsaturated copolymers of acrylonitrile and butadiene. It contains 20–40% acrylonitrile.

## 2. Experimental

### 2.1. Materials

Acrylonitrile butadiene rubber (NBR) with a molecular weight of  $1.8 \times 10^5$  g/mol and 27% acrylonitrile content was supplied from RRI, Kottayam. One repeating unit of NBR is



Reagent grade iodine is further purified by sublimation followed by recrystallisation. Gr grade chloroform (Merck) is used as received.

### 2.2. Conjugation reaction in solution

The iodine doping reaction of the as received polymer is carried out by dissolving the polymer sample and iodine at a determined ratio of  $[\text{C}=\text{C}]/[\text{I}_2] = 8$  in chloroform and sealed under nitrogen. NBR concentration is 0.025 g/ml and of iodine is 0.014 g/ml. The thin films of doped solution are spin coated on glass and quartz plates at different time periods and directly used for UV/VIS, FT-IR and conductivity measurements.

### 2.3. Reaction in solid films

A viscous solution of NBR in chloroform is spin coated on quartz and glass plates so as to obtain films of uniform thickness and dried under vacuum. The dried films are placed in an evacuated glass chamber and exposed to iodine vapors. The extend of reaction with iodine vapor is controlled primarily by the exposure time of films. The excess unreacted iodine is pumped off under dynamic vacuum prior to spectroscopic analysis.

### 2.4. Spectral studies

UV/VIS measurements of the films coated on quartz plates are recorded on a Systronics Make UV/VIS spectrometer in the range between 200 and 900 nm. Films of the as received samples are found to be transparent between 200 and 900 nm. Fourier transform Infra red (FTIR-ATR) spectra are measured on a FT-IR Impact 410 Spectrometer in the range of 4000–625  $\text{cm}^{-1}$ .

### 2.5. DC resistivity measurements

The resistivity measurements of doped films are carried out using the standard two wire and four wire methods on Keithley electrometer 6514 and Keithley multimeter 2000, respectively. For this, four contact points at equal distances of 3 mm are coated with silver. For two-probe measurement the test current is forced through the leads and the resistance is measured from the voltage drop developed across the points. For low resistance measurements, four-wire connection is used. In this configuration a suitable voltage is applied between two contacts and the resulting current is measured across the other two points. The measurement set-up is fully automated and controlled by a computer programme.

### 2.6. Swelling studies

The films are peeled out from the glass plates and are weighed and swelling experiments are performed by immersing them in chloroform contained in test bottles having airtight stoppers. The samples are periodically removed from the solvent and weighed quickly on an electronic balance (Sartorius) to an accuracy of 0.1 mg. The procedure is repeated until an equilibrium is attained after 3 days.

The swelling ratio [12] is given by  $Q = \text{Swollen weight} - \text{dried weight} / ((\text{original weight} \times 100) / \text{formula weight})$

## 3. Results and discussion

The iodine induced conjugation reaction of natural rubber in solution has been previously studied [7,13–15]. Analogous reaction sequences can also apply to the reaction between iodine and NBR in the solid state, as attested by the conductivity measurements and UV/VIS and FT-IR spectral analysis before and after doping.

Fig. 1 shows the time dependence of four probe electrical conductivity for the NBR during the reaction with iodine in chloroform at  $[\text{C}=\text{C}]/[\text{I}_2] = 8$  at room temperature. The observed kinetic curve resembles the reaction between iodine and NR in toluene [9] suggesting a similar reaction mechanism in both cases. As can be seen in the figure, the conductivity of NBR increased by eight orders of magnitude with increase in reaction time. We had found that in the case of SBR iodine doping yielded a maximum conductivity of  $10^{-1}$  S/cm for a doping period of 20 days [1]. But it is interesting to note that in the case of NBR it took a longer doping period (58 days) to get maximum conductivity of  $10^{-2}$  S/cm (Fig. 1). The possible

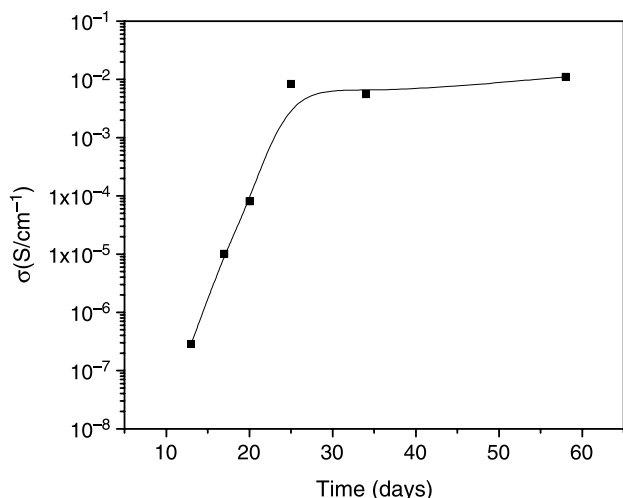


Fig. 1. Electrical conductivity of iodine doped NBR film  $[C=C]/[I_2]=8$  for different time intervals.

reasons for this contrasting behaviour has been discussed in the latter part of this work.

As shown in Fig. 2, the pristine film is colorless over the range of wavelengths from 230 to 700 nm as would be expected for an isolated double bond structure. The conjugation of the lone pair on the nitrogen atom of the  $-CN$  group has shifted the absorption maximum from the isolated double bond value of 190–260 nm [16]. A very low intensity band in the 270–350 nm region corresponds to the  $n-\pi^*$  transition of  $-CN$  group [16] along the polymer backbone. As the reaction with iodine proceeds the colorless NBR films turn pale yellow–dark yellow–red with the increase in doping period. The optical density increased strongly throughout the wavelength region, accompanied by the appearance of broad peaks between 300 and 500 nm, with the increase in doping period. A decrease in the absorption at 262 nm corresponds to the decrease in the concentration of isolated  $C=C$  units on doping [15,16].

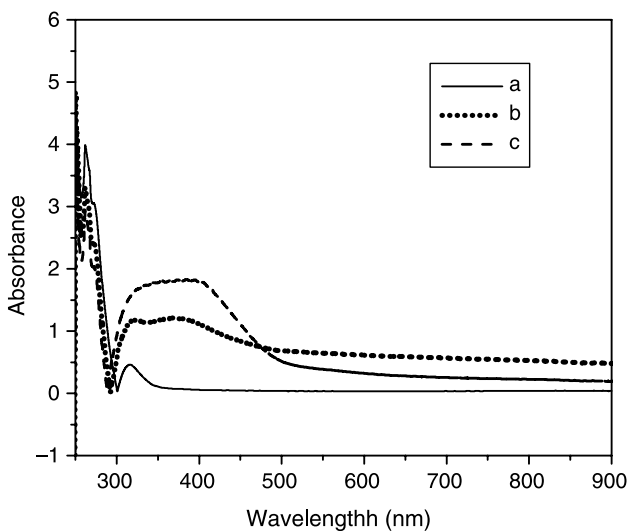


Fig. 2. The UV/vis spectra of iodine-doped NBR films (with molar ratio 2.68) doped for different time intervals by solution method. (a) Undoped (b) after 25 days (c) after 58 days.

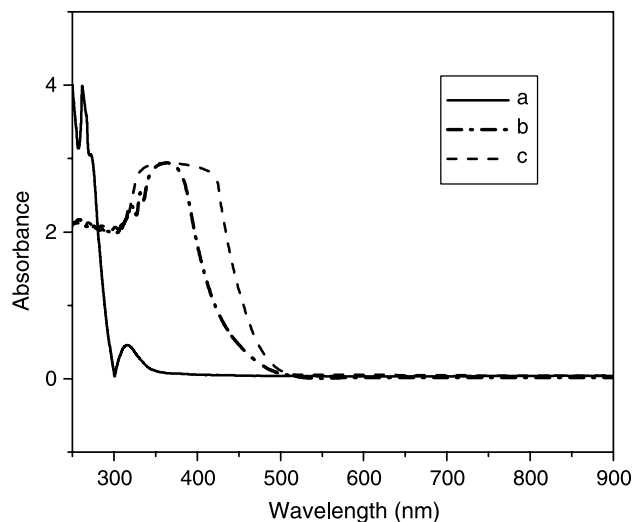


Fig. 3. The UV/vis spectra of iodine-doped NBR films doped for different time intervals by gas phase method. (a) Undoped (b) after 5 days (c) after 7 days.

The reaction in solid state (Fig. 3) are also closely analogous to those reported for doping reactions of homopolydienes. The observed absorption peaks have been attributed to charge transfer complexes formed between the newly produced conjugated sequences and iodine. The above result suggests a similar mechanism for the iodine-induced conjugation reaction in homopolydienes and non-conjugated diene segments of the copolymers [6,7,13,15]. On comparing the UV/VIS spectra of SBR (Fig. 4) [1] and NBR (Fig. 3), for SBR, absorption bands extending to near infrared region are observed. This absorption is essentially due to stronger charge transfer complexes, which is stabilized by the conjugation with electron rich benzene group along the polymer backbone of SBR. For NBR the absorption bands limit to visible region (Fig. 3), i.e. the possibility of transition from short polyene  $I_2$  charge transfer complexes to  $I_2$  charge transfer complexes with longer polyenes is less frequent. In the case of another elastomer polybutadiene it has been reported that strong absorption in the visible region resulted in fluorescence emission [17]. It would

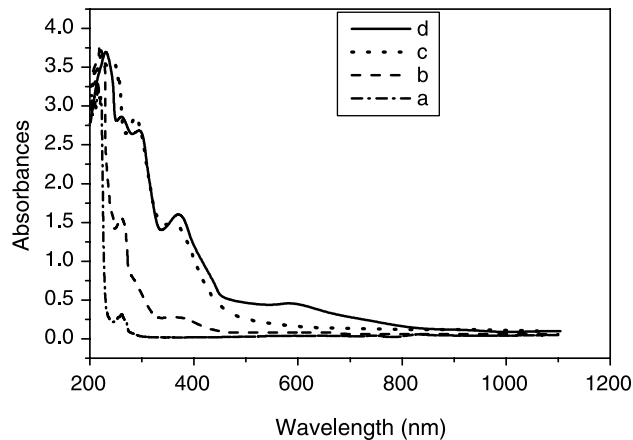


Fig. 4. The UV/vis spectra of iodine-doped SBR films doped for different time intervals by gas phase method. (a) Undoped (b) after 2 days (c) after 12 days (d) after 13 days.

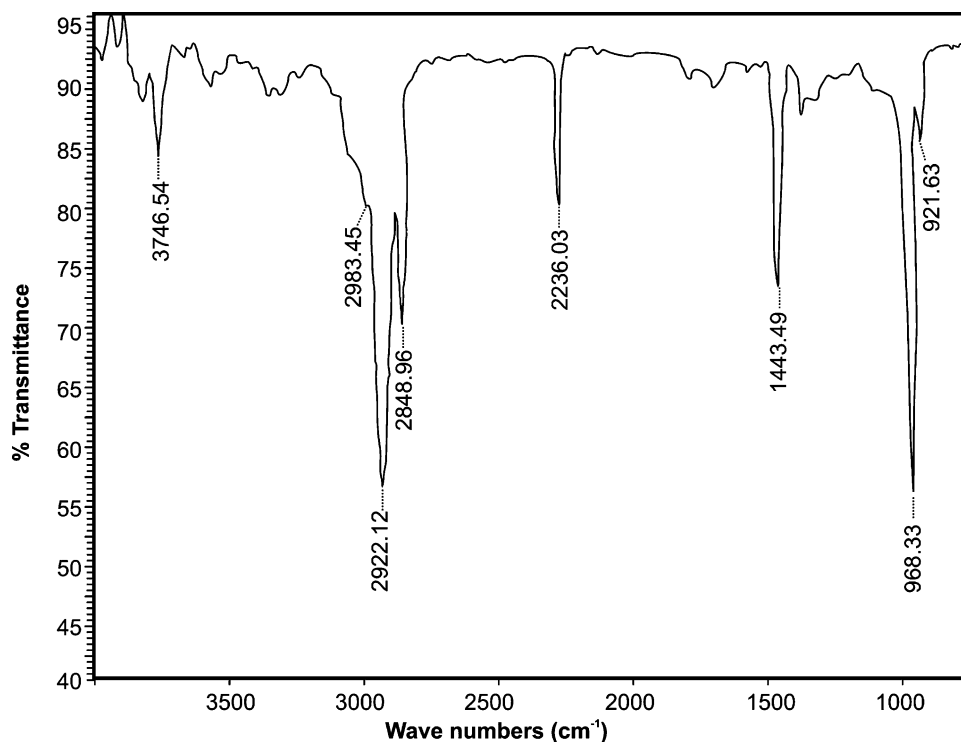


Fig. 5. FTIR-ATR spectra of pristine NBR film.

be interesting to study whether NBR would produce any such emission as NBR also strongly absorbs in visible region.

The doping reactions are confirmed by FTIR-ATR spectra of NBR recorded before and after doping with iodine. For undoped films, as shown in Fig. 5, the characteristic  $-\text{CH}_2$  and  $-\text{CH}$  stretching bands in the region of  $2700\text{--}3000\text{ cm}^{-1}$  [18] as well as the peak at  $968\text{ cm}^{-1}$  attributable to the  $=\text{CH}$  out of plane (bending) deformation indicates the trans counterpart butadiene segment of NBR [18]. After reacting with iodine (Fig. 6) the peak at  $1650\text{ cm}^{-1}$  associated with the stretching vibration of isolated  $-\text{C}=\text{C}-$  bonds shows a decrease in intensity with new bands appearing at lower frequencies of  $1540\text{--}30\text{ cm}^{-1}$  which corresponds to the possible unsaturated conjugation formed as the result of doping reaction [18]. These changes in the FTIR-ATR spectra are consistent with the addition of iodine to  $\text{C}=\text{C}$  bonds along the trans counterpart of the butadiene segment of the NBR chain. The band at  $2236\text{ cm}^{-1}$  characteristic of  $-\text{CN}$  stretching vibration remains intact even after the doping reaction. However, unlike iodine doping in polybutadienes [18] the peak at  $968\text{ cm}^{-1}$  corresponding to  $=\text{CH}$  bending vibration does not decrease much showing that the flexibility is retained even after doping for longer time periods. This may be due to the lower concentration of allyl groups in NBR compared to homopolydienes which are proposed to be the active site for cross linking reactions. After compensation with  $\text{NH}_3$  (Fig. 7) almost all of the absorption bands characteristic of the pristine NBR are recovered and this proves the reversibility of the doping reaction.

The optical band gap ( $E_g$ ) of doped NBR films are calculated using the Tauc relation  $\alpha h\nu = A(h\nu - E_g)^n$ , where  $A$

is constant,  $h\nu$  is the photon energy,  $E_g$  is the band gap and  $n$  is an index which assumes the values  $1/2$ ,  $3/2$ ,  $2$  and  $3$  depending on the nature of electronic transition responsible for the absorption.  $n=1/2$  is taken for an allowed direct transition [19]. Using spectral plots and photon energy curves between  $(\alpha h\nu)^2$  and  $h\nu$  band gaps of various samples are evaluated. Figs. 8 and 9 gives such plots for the sample film doped (solution phase) for 58 days. The extrapolation of straight line to  $(\alpha h\nu)^2=0$  gives the value of direct band gap. The band gap is evaluated to be  $2.3\text{ eV}$ . Undoped elastomers generally possess a high band gap of  $\sim 5\text{--}6\text{ eV}$ . Thus a decrease of band

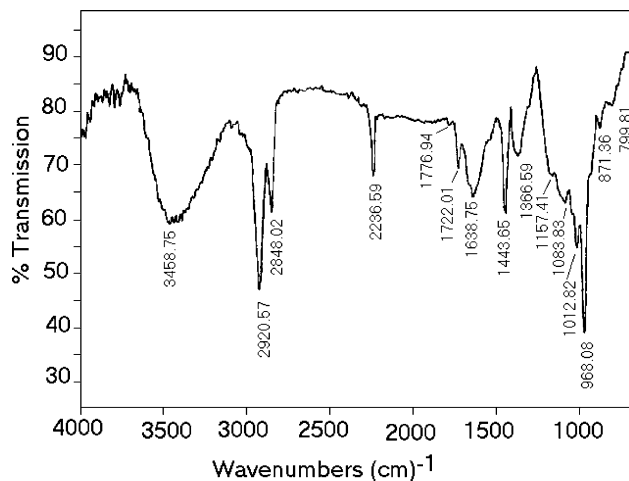


Fig. 6. FTIR-ATR spectra of  $\text{I}_2$ -doped NBR films doped for 13 days at a molar ratio of 8.

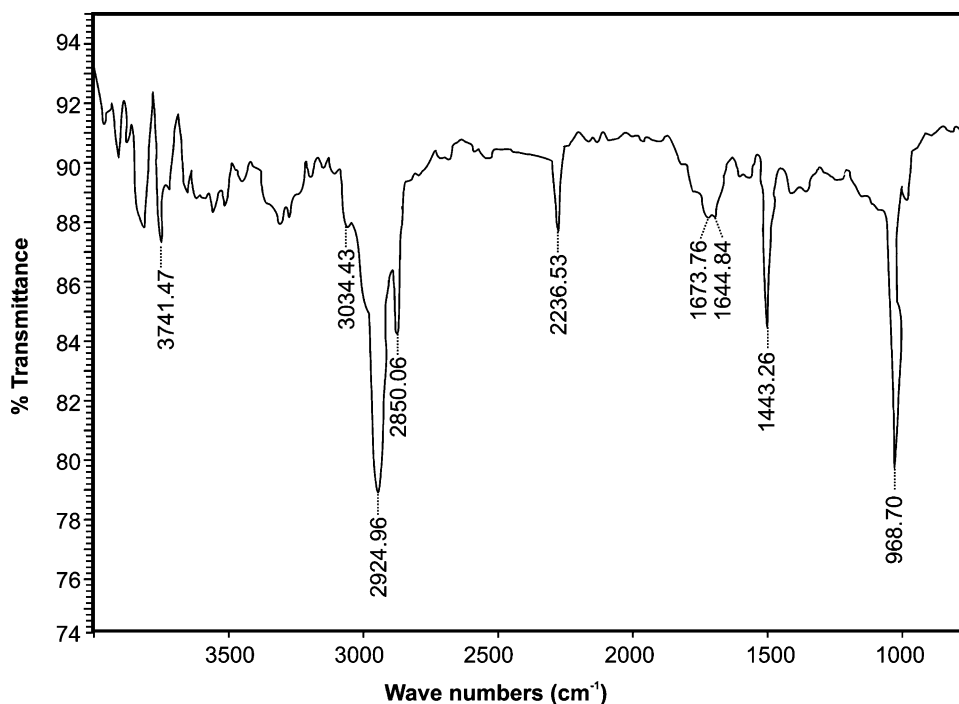


Fig. 7. FTIR-ATR spectra of  $I_2$ -doped NBR films after ammonia compensation.

gap indicates the transition of NBR from an insulator to a semiconducting polymer on doping and conjugated sequences is responsible for the observed transition.

On the basis of the results, it is clear that the doping reaction involves the double bond shift reaction on the butadiene segments of the NBR chain by the addition of iodine to double bond followed by the E-2 elimination of HI as proposed for *trans*-polybutadienes [11], Polyisoprene [9] and other dienes and is shown in Scheme 1. The iodine atoms interact with the conjugated  $-C=C-$  groups in the NBR chain and the charge transfer takes place to generate outer and inner charge transfer complexes as proposed in Scheme 2. The broad absorption

bands between 300 and 500 nm (Figs. 2 and 3) suggest the generation of  $I_3^-$  ions through a transformation of the outer charge transfer complexes to inner ones. The mechanism is similar to that by which  $I_3^-$  ions are generated through iodine doping of polyacetylene (PA) in solid state [11]. The contribution of the charge transfer complexes is that it facilitates the generation of  $I_3^-$  ions, which stabilizes the positive ions responsible for the conductivity of the polymer.

As indicated earlier, the conjugation reaction in co-polymers, are characterized by longer doping period indicating a slow kinetics for the reactions. This is expected since compared to homopolydienes, in co-polymers the  $C=C$  bonds

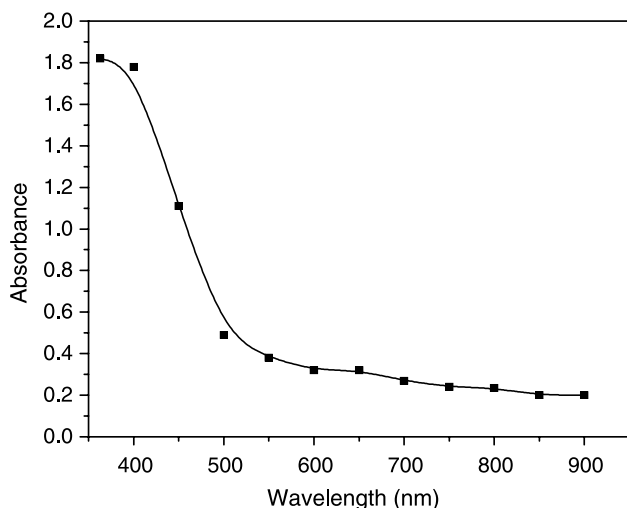


Fig. 8. Absorbance versus wavelength for NBR samples doped for 58 days at  $[C=C]/[I_2]=8$ .

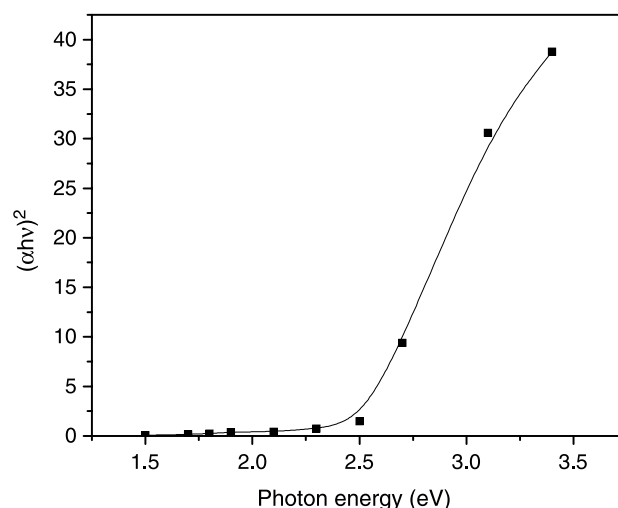
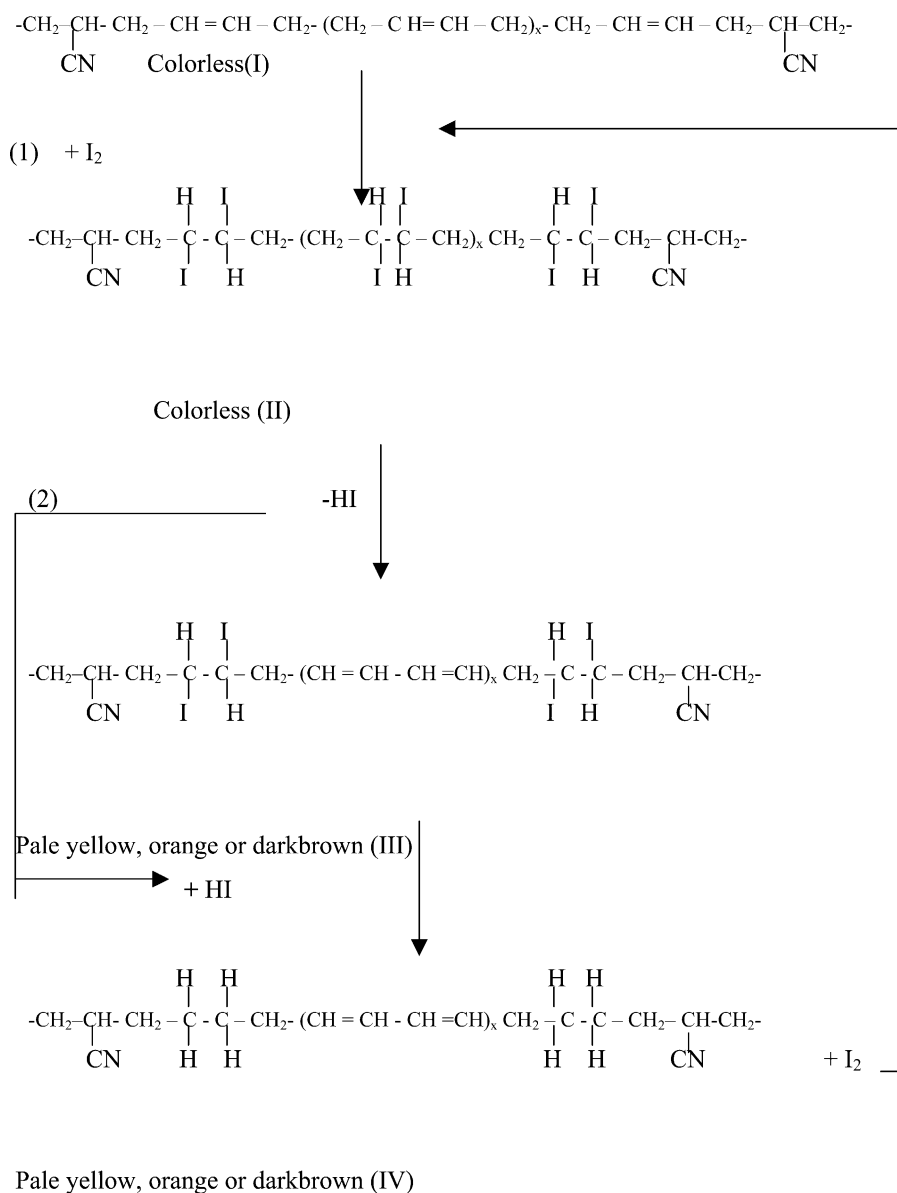


Fig. 9.  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for NBR sample doped for 58 days at  $[C=C]/[I_2]=8$ .

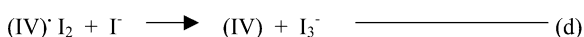
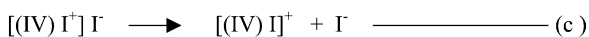
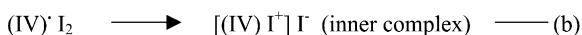
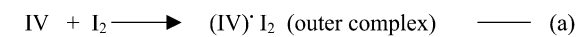


Scheme 1. Doping mechanism in NBR.

are less frequent. Moreover, the activity of iodine is affected by the nature of the groups attached to the double bond. Thus the methyl group present in the natural rubber molecule increases activity [20] whereas no such electron releasing groups are present around the double bond in the butadiene segment of

the SBR or NBR polymer backbone. This explains the low rate of doping in co-polymers.

Pure NBR is soluble in CHCl<sub>3</sub>, while the doped samples remain insoluble in the same solvent with an increase in swelling ratio with the increase in doping period (Table 1). This indicates that doping reaction also results in cross-linking between the chains making the film more flexible and strong. In contrast iodine doping in polyisoprene [9] and polybutadienes [11], makes the material rigid as a result of excessive



Scheme 2.

Table 1  
Change in swelling ratio with doping period

Doping period (days)	Swelling ratio <i>Q</i>
13	1.36
25	2.61

cross-linking. This is because in the case of NBR interchain cross linking is considerably less because the concentration of allyl radicals responsible for the cross linking in NBR is low.

The presence of –CN groups along the NBR chain is expected to decrease the activity of iodine on the double bonds. However, the positive results for doping reaction suggests that the low concentration of –CN group compared to –C=C– do not much affect the doping reaction but it may cause a partial influence which explains the larger optical band gap and lower maximum conductivity as compared to SBR [1] and other dienes [13–15].

#### 4. Conclusion

We successfully synthesized conductive films from NBR by means of iodine doping as in the case of SBR and homopolydienes. The electrical conductivity, optical absorption and FT-IR measurements at different doping periods are made. The conductivity increases by eight orders of magnitude and the UV/VIS and FT-IR spectra indicate the formation of possible unsaturated conjugation along the polymer backbone. These clearly show that the overall doping mechanism is similar to that for homopolydienes, but with a characteristic difference of longer doping period, i.e. slow reaction rate, which is attributed to the presence of the second component along the polymer backbone. Moreover, the flexibility is retained to a greater extent even after doping for a longer time period. Thus it can be concluded that iodine-doping reaction is possible for any unsaturated copolymer chain irrespective of the nature of saturated monomer segment.

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