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A novel intrinsically conducting polymer for optoelectronic applications from Acrylonitrile-Butadiene Rubber (NBR)

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High intrinsic electric conductivity has been developed in the non-conjugated copolymer Acrylonitrile-Butadiene Rubber (NBR) by doping with Antimony Pentachloride ($SbCl_5$). With increase in the rate of doping conductivity is found to increase by 9 orders of magnitude followed by a color change of NBR films from colorless to dark brown. Also an effort has been made to compare the effects of $SbCl_5$ doping with iodine doping in NBR. Comparison of spectral studies, conductivities at different doping periods and the resulting band gap values of I_2 and $SbCl_5$ doped NBR clearly indicated the efficiency of $SbCl_5$ doping over I_2 doping. The underlying mechanism of doping in both cases has also been discussed.

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Keywords: $SbCl_5$ doping, Nonconjugated polymer, Acrylonitrle-Butadine Rubber (NBR)

1. Introduction

Conducting polymers form a new class of materials that can be doped to vary from semiconductor to metallic regime and are proved to be potential candidates for device applications, mainly in opto-electronic device fabrication [1-4]. Most of the conducting polymers are characterized by long series of alternating single and double bonds. This conjugated structure not only provides a continuous conduction path along the polymer backbone but also facilitates the generation of charge carriers upon doping with appropriate electron acceptors (lewis acids, I_2 etc.) or electron donors (SodiumNaphtalide etc) [5].

Thakur in 1988 reported that [6] iodine doping of cis-1,4-polyisoprene, a non conjugated organic polymer with isolated double bonds, showed characteristic color changes responsible for the formation of conjugated sequences with conductivity increase of about ten orders of magnitude. This gives the possibility of a new class of non-conjugated conducting polymers. Later Liming Dai and coworkers demonstrated that [7,8] double bond shift reactions occur in the carbon chain in these materials as a result of doping and this facilitates the charge transfer complex formation from the conjugated segments and dopant in solution. Since then, various non-conjugated homopolydienes such as cis and trans 1, 4 – polybutadiens, 2, 3-dimethyl butadiene etc are reported to become dark in color and conductive on doping reactions [9-11]. A similar reaction had been carried out in cross-linked natural rubber (cis 1,4-polyisoprene) recently [12] and the mechanism of doping reaction is analogues to that observed for the above polymers.

In this context an attempt has been made here to dope Acrylonitrile Butadiene Rubber (NBR) with Antimony Pentachloride ($SbCl_5$). NBR is a copolymer of acrylonitrile and butadiene. It is an insulating material in the crude and in the vulcanized form. NBR pocesses good chemical and oil resistance and are usually used in applications where these properties are particularly important [13]. This study reports the effect of doping NBR with $SbCl_5$ and also makes a comparative investigation of the effects of $SbCl_5$ doping and I_2 doping on NBR.

2. Experimental section

2.1 Materials

Acrylonitrile Butadiene rubber with a number average molecular weight of 1.8×10^2 Kg/mol is supplied from Rubber Research Institue , Kottayam and is used as received. The acrylonitrile- butadiene ratio is estimated to be 27: 73. Dopant $SbCl_5$ (Aldrich) is a colorless liquid at room temperature and this is also used as received. Chloroform and Carbon tetra chloride (Merck) are used without further purification.

2.2 Sample preparation

2.5×10^{-4} Kg of NBR is dissolved in $10\times10^{-6}m^3$ chloroform to form a clear viscous solution. From this solution thin films of NBR are fabricated on quartz and glass substrates by spin coating method. The films are dried under vacuum. $SbCl_5$ solution in CCl_4 (0.2×10^{-6} m^3 $SbCl_5$ /10×10^{-6} m^3 CCl_4) is used as the dopant. NBR films are kept immersed in this solution for various time periods of 0,48,96 and 196 hrs.

2.3 Characterization

UV/Vis and FTIR spectral studies are employed to characterize the samples. The absorption spectra are

recorded using UV/Vis Spectrophotometer in the wavelength range 300 to 900 nm. FTIR spectroscopic measurements are performed using a Nicolet Spectrometer in the range of 500- 3000 cm $^{-1}$. Conductivity of the doped samples are measured using Keithly 6514 Electrometer and Keithly 2000 DMM at room temperature using two probe and four probe methods.

3. Results and Discussion

The dopant $SbCl_5$ is more electronegative than iodine [14], therefore it is supposed to bring about more efficient reactions with the –C=C- bonds of the copolymer. It is seen that $SbCl_5$ doping leads to gradual color changes in the NBR film from colorless to dark yellow and finally to reddish brown at different time periods of 96 hrs and 168hrs (7 days). Our earlier reported [15] studies showed that in solution doping reactions of NBR with iodine, similar color changes required comparatively longer doping periods of 13 days, 25 days, 56 days respectively. Fig. 1 gives the electrical conductivities of iodine doped and $SbCl_5$ doped NBR samples as a function of doping period. In iodine doped NBR the conductivity saturates at 10^{-2} (S/cm) corresponding to a doping period of 56 days while in the case of $SbCl_5$ doping the conductivity reaches 10^{-2} S/cm after a comparatively lower period of seven days. From this wide difference in the doping periods for the two dopants to attain maximum conductivity it is evident that $SbCl_5$ is a more efficient dopant. The enhanced reactivity of $SbCl_5$ can be attributed to the presence of more reactive chlorine atoms, while iodine is weaker as an acceptor to carry a sudden reaction in NBR backbone.

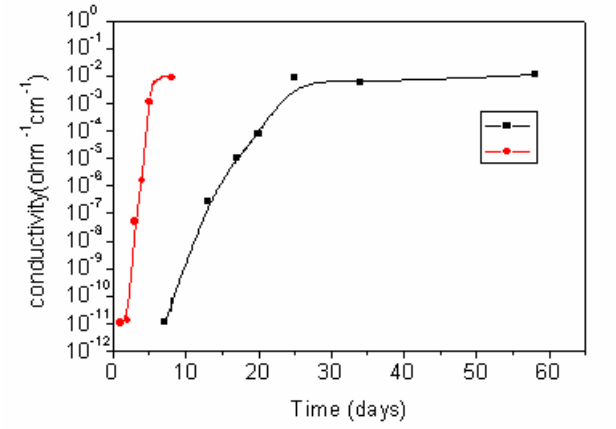


Fig. 1. *Electrical conductivity as a function of doping time for doping with —●— $SbCl_5$ and iodine —■— as dopants.*

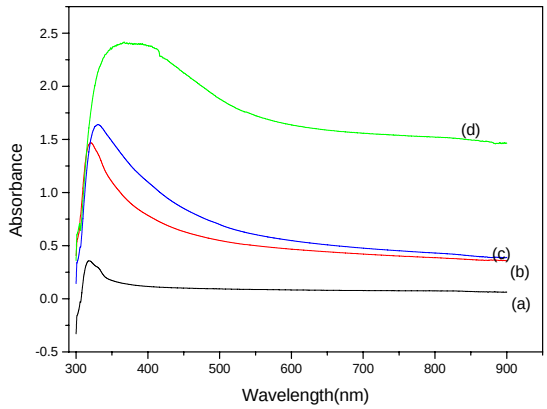


Fig. 2. The UV/Vis spectra of $SbCl_5$ -doped NBR films doped for different time intervals by solution method. a) Reference b) 4 hours c) 3 days d) 7 days.

UV/VIS spectrum of $SbCl_5$ doped samples at different doping periods is shown in Fig. 2. Except a small absorption peak between 270-300 nm which corresponds [15] to the n- π^* transition of –CN group along the polymer backbone, the pristine film shows no other absorption in the wavelength region of 270-900 nm. It is clear from the spectrum that the absorption increases with increase in doping period with absorption edge extending towards near infrared region. This is essentially due to [8] the formation of stronger charge transfer complexes upon heavy doping. Even at a small doping period of 4 hours strong absorption peaks are formed, which indicates that maximum conjugation is achieved at the onset of the reaction resulting in the formation of longer polyene sequences at the initial reaction stage itself.

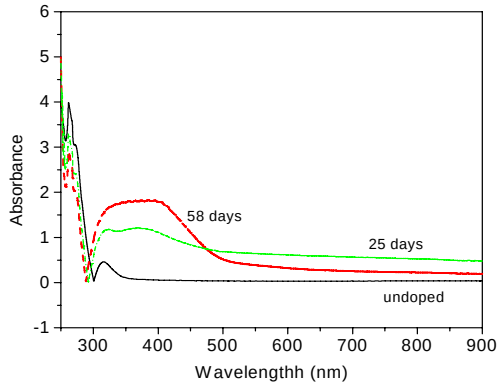


Fig. 3. *The UV/Vis spectra of iodine-doped NBR films (with molar ratio 8) doped for different time intervals by solution method. a) Undoped b) After 25 days c) After 58 days.*

In the UV/Vis spectra of iodine doped NBR, given in Fig. 3, the absorption is seen to be limited to the visible region even after a long doping period. The iodine-doped NBR films showed a much higher optical density than the $SbCl_5$ doped films. This is due to the strong absorption of iodine, which is present in the polymer either in the form of I_2 molecules or I_3^- and I_5^- ions. But the color of the $SbCl_5$ doped samples must be originating from the optical absorption of the oxidized polymer itself [16].

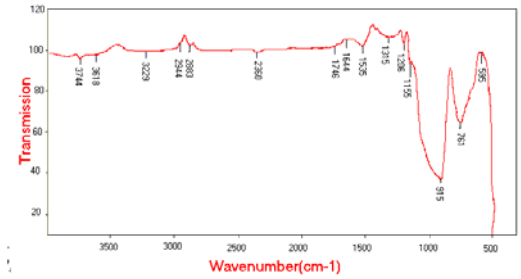


Fig. 4. FTIR Spectra pristine NBR film.

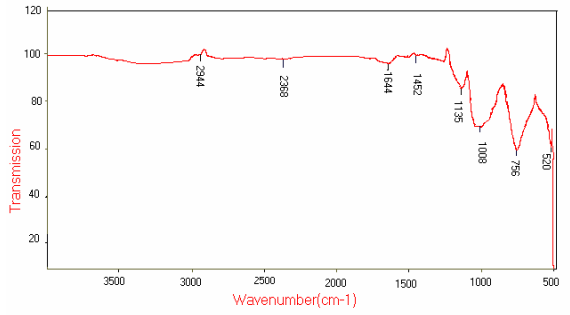


Fig. 5. FTIR Spectra of SbCl5 -doped NBR film of 7 days.

Fig. 4 and 5 represent the FTIR spectra of pristine NBR and 72 hours $SbCl_5$ doped NBR respectively. The changes in FTIR spectra reveals the addition of $SbCl_5$ to -C=C- bonds of NBR. The significant loss of intensity of the peak at 1644cm^{-1}, which originates [17] from the stretching vibration of isolated -C=C- bonds of pristine NBR, is a clear indication of polar addition of $SbCl_5$ to polybutadiene segments. A new band, which appeared at 520cm^{-1} [17], may be assigned to the C-Cl stretching vibration. It can be seen that this band is originally got shifted from the normal absorption frequency region of 800-600cm^{-1}due to the influence of dipolar –CN group of acrylonitrile component in the copolymer. The bands at 762 and 916, characteristic of =CH out of plane (bending) deformation of cis and trans butadiene segments of pristine NBR [18], significantly decrease and new bands are formed at lower frequencies. The decrease in intensity indicates a loss of flexibility and embrittlement of NBR due to the formation of charge transfer complexes between the newly introduced conjugated sequences and dopant ions [19].

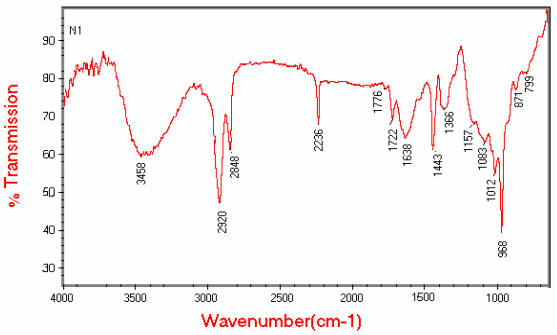


Fig. 6. FTIR-ATR spectra of I_2 doped NBR films doped for 13 days at a molar ratio of 8.

Fig. 6 shows the FTIR-ATR spectrum of I_2 doped NBR. It is seen that, a new peak is formed at 1638cm^{-1} along with new bands at lower frequency range of 1540-30cm^{-1} [15]. This is a clear indication of the addition of I_2 to isolated -C=C- bonds along NBR to form conjugated sequences.

In homopolydienes like polybutadiene, polyisoprene etc doping results in the addition of dopant molecules to double bonds along the polymer backbone. This cause a double bond shift reaction accompanied by the formation of outer and inner charge transfer complexes [8-10]. From the spectral results it is clear that a similar type of conduction mechanism is occurring in both I_2 and $SbCl_5$ doped NBR samples. Mechanism of conduction in I_2 doped NBR had been described previously by us [15]. Conduction mechanism in $SbCl_5$ doped NBR can be explained through the scheme I and II. Doping reaction involves the addition of $SbCl_5$ to polybutadiene segments of NBR followed by the E-2 elimination of HCl and H_2SbCl_3 [19]. This reaction results in the formation of conjugated sequences along NBR. Further, there occurs addition of HCl to the polymer chain by a free radical mechanism [20]. Cl atom of $SbCl_5$ react with the newly formed conjugated sequences in NBR chain and charge transfer occurs between conjugated segments and dopant ions with the formation of outer and inner charge transfer complexes. This is explained in scheme II. Cl_3^- ions are produced during charge transfer reaction. Presence of Cl_3^- ions in polymers is supported by the findings of Shirakawa et al with the help of Raman spectral studies in $SbCl_5$ doped polyacetylene [21].

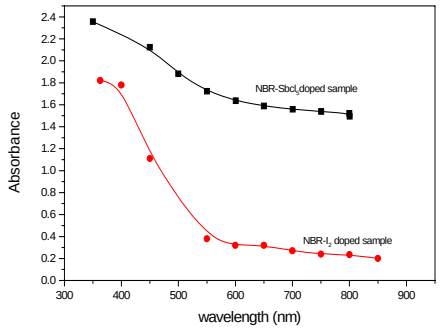


Fig. 7. Absorbance verses wavelength graph comparing NBR film doped with $SbCl_5$ after 7 days and NBR films doped using iodine after 58 days.

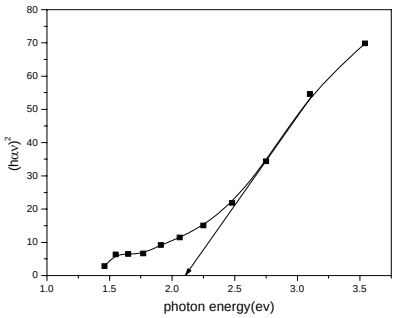


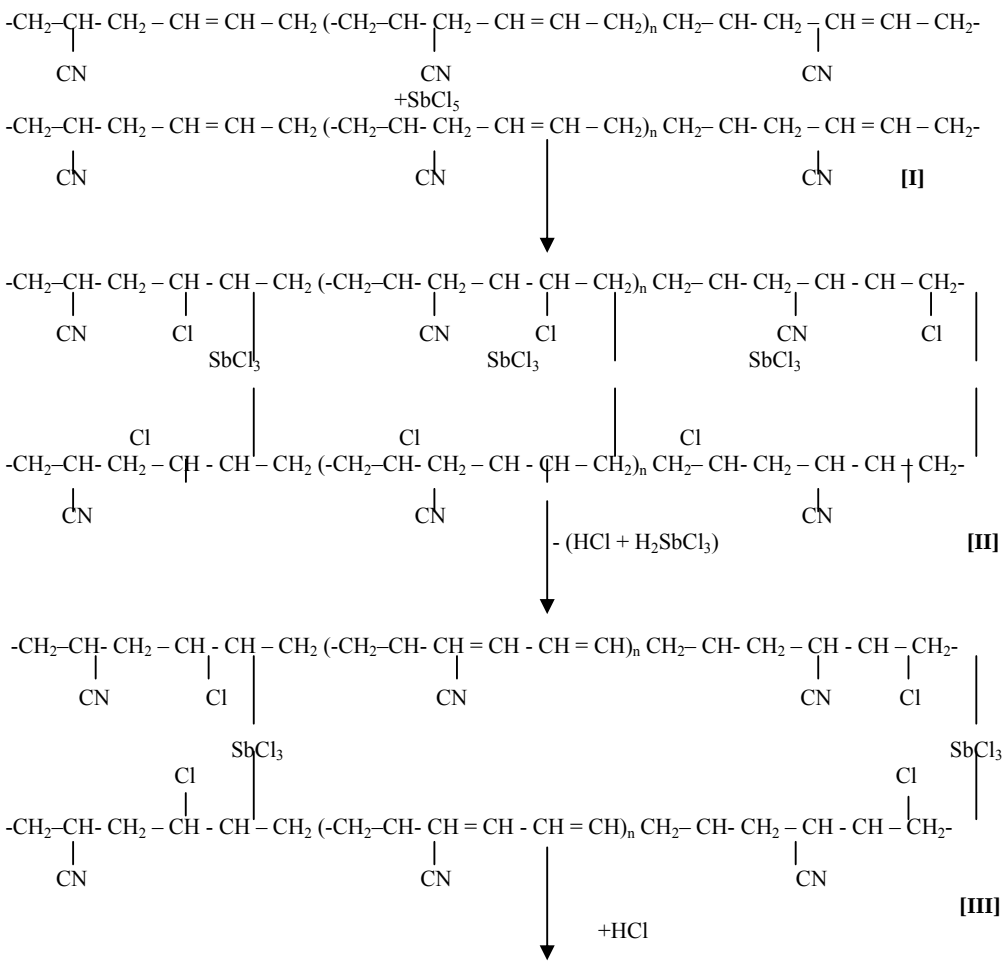
Fig. 8. $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for NBR sample doped with $SbCl_5$ for 7 days.

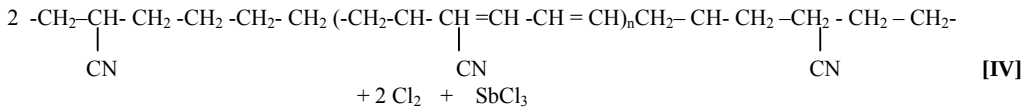
The optical band gap (E_g) of doped NBR film is evaluated using the relation $\alpha h\nu = A (h\nu - E_g)^n$, where A is constant, hν is the photon energy, Eg is the band gap and n is an index which assumes the values ½, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption. n=1/2 is taken for an allowed direct transition [22]. Using spectral plots and photon energy curves between $(\alpha h\nu)^2$ and hν, band gaps of various samples are evaluated. Figs. 7 and 8 gives such plots for 7 days $SbCl_5$ doped NBR film. The band gap is evaluated to be 2.1 eV while that for iodine doped NBR found to be 2.3 eV [15]. A decrease of band gap from insulator to semi conducting range underline the formation of conjugated sequences in the polymer.

4. Conclusion

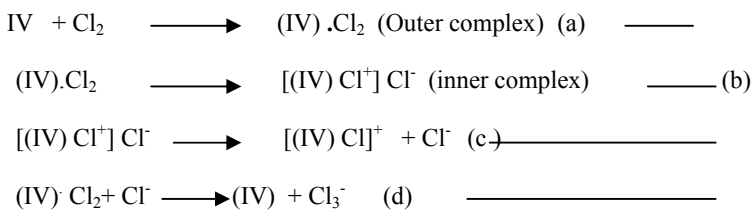
Thin films of NBR with a conductivity of about 10^{-2} S/cm have been prepared using $SbCl_5$ as dopant. It is clear from the comparative study of $SbCl_5$ and I_2 doping that $SbCl_5$ is more efficient in doping the copolymer than I_2. $SbCl_5$ doped NBR reaches maximum conductivity within a correspondingly short period of time than that of iodine doped one. This indicates that by selecting appropriate dopants the rate of doping can be controlled. However the mechanism of electrical conduction in both cases involves mainly the formation of charge transfer complexes via double bond shift reactions as observed in the case of homopolydienes.

Doping Mechanism in NBR





Scheme 1



Scheme 2

References

[1] J. Wang, Y. L. Bunimovich, G. Sui, S. Savvas, J. Wang, Y. Guo, J. R. Heath, H. –R. Tseng, Chem. Commun, 3075-3077 (2006).

[2] A. K. Narula, R. Singh, S. Chandra, Bull. Mater.Sci, **23**(3), 227 (2000).

[3] E. Dalas. J. Mater. Sci . **27**, 453 (1997).

[4] J. Anand, S. Palaniappan, D. N. Sathya Narayana, Prog. Poly. Sci. **23**, 993 (1998).

[5] J. C. W. Chien, 'Polyacetylene: Chemistry, Physics and Material Science', Academic Press, New York. (1984)

[6] M. Thakur, 'A Class of Conducing Polymers having non-Conjugated Backbone', Macromolecules. **21**, 661 (1988).

[7] L. Dai, J. W. White. Polymer. **32**(12), 2120 (1991).

[8] L. Dai, The journal of Physical Chemistry. **96**(15), 6469 (1992).

[9] P. Calvert., Nature. **333**, 296 (1988).

[10] L. Dai, A.W. H. Mau, H. J. Griesser, D. A.Winkler, 'Conducting Polymers from Polybutadiene Molecular Configuration: Effects on The Iodine Induced Conjugation Reactions', Macromolecules, **27**(23), (1994).

[11] M. D. da Silva, L. C. M. Miranda, Physical Review B**49**, 18 (1993).

[12] R. Sreeja, P. Predeep, R. Alex, P. D. Sharma. Progress in Rubber, Plastics and Recycling Technology. **20**(3), (2004)

[13] M. R. Vallim, M . I .Felisberti, M. -A. De Paoli, J. Appl. Polym. Sci. **75,** 677 (2000).

[14] Guo-Qing Yu, M. Thakur, J. Polym. Sci. **32**, 2104 (1994).

[15] R. Sreeja, S. Najidha, Remya Jayan, P. Pradeep, M. Mazur, P .D. Sharma. Polymer**,** 1-7, 0. 09. 024, (2005).

[16] B. Ticke, S. A. Zahir., Polymer. **35**, 2467 (1995).

[17] W. Kemp, Organic Spectroscopy. Mac Millan Publishers Ltd: 150-159 (1978).

[18] L. J. Bellamy, Material Letters. **59**, 3431 (2005).

[17] S. W. Benson, A. N. Bose. J. Am. Chem. Soc. **85**, 1385 (1963).

[18] H. Shirakawa, T. Sasaki, S. Ikeda, Chem. Lett. 1113 (1978).

[19] G. P. Joshi, R. Mangal, N. S. Saxena, T. P. Sharma, Indian Journal of Pure & Applied Physics. **40**, 297 (2002).

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