Polymer Vol. 37 No. 15, pp. 3215–3218, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/\$15.00+0.00

Electrically conductive polymers from poly(*N*-vinylimidazole)

Zuhal Küçükyavuz*, Savas Küçükyavuz and Nahid Abbasnejad
Department of Chemistry, Middle East Technical University, 06531-Ankara, Turkey
(Received 9 June 1995; revised 13 December 1995)

Poly(*N*-vinylimidazole) was synthesized by free radical polymerization. It was quaternized with methyl iodide. The samples were doped with iodine and borontrifluoride. Products were characterized by elemental analysis, Fourier transform infra-red spectroscopy and differential scanning calorimetry techniques. The maximum electrical conductivities achieved were 10^{-4} S cm^{-1} for BF_3-doped and for I_2-doped QPVI. The decrease of electrical conductivity in open atmosphere with time was also studied to understand the stability of doped polymers. Temperature dependence of electrical conductivity exhibits a semiconductor behaviour. Copyright © 1996 Elsevier Science Ltd.

(keywords: poly(*N*-vinylimidazole); BF_3 doping; I_2 doping)

INTRODUCTION

Conducting polymers have received considerable attention in the past few decades. Potential advantages of conductive or semiconductive polymers lie in their light weight and in the ease of their synthesis and fabrication. But many electrically conducting polymers which have been described to date have undesirable characteristics such as insolubility, poor processibility and poor atmospheric stability[1]. Various methods have been used to improve the processibility of conducting polymers[2] such as preparation of blends[3] or synthesizing block or graft copolymers in which one component is a potentially conductive polymer and the other component increases the solubility and improves the mechanical properties and the processibility.

In our previous studies on conducting polymers we investigated electrical properties of poly(4-vinylpyridine)-poly(dimethylsiloxane) block copolymers doped with tetracyanoquinodimethane (TCNQ) and iodine[4,5]. In these systems a poly(4-vinylpyridine) block, which makes charge transfer complexes with dopants, constitutes the continuous conducting phase whereas the presence of an elastomeric insulating poly(dimethylsiloxane) block does not greatly affect the conductivity, but improves the mechanical and thermal properties of the conducting structure.

The polymerization and solution properties of imidazole based polymers were investigated previously[6,7]. The catalytic activity of polyimidazoles has been the subject of extensive studies[8,9]. Poly(*N*-vinylimidazole) (PVI), which is soluble in several organic solvents also seemed promising to us to transform into a conducting polymer, as it has an electron-rich aromatic ring with heteroatoms, similar to pyridine, pyrrole and thiophene etc., and therefore can possibly make charge transfer complexes with electron acceptors.

The present investigation concerned conductive properties of PVI doped with iodine and boron trifluoride.

EXPERIMENTAL

Polymer synthesis

N-Vinylimidazole was a produce of Merck Co. It was purified by vacuum distillation just before use.

Polymerizations were carried out under high vacuum using azobisisobutyronitrile as initiator and benzene as solvent at a constant temperature of 60°C. The polymer was collected by filtration and was finally dried in an vacuum oven at 50°C. Molecular weight as determined by intrinsic viscosity measurements in methanol, was 2×10^5.

Preparation of polymer films

Transparent and homogeneous films of PVI were prepared from 1% (w/v) methanol solution on a clean mercury surface. For quaternized samples, films were cast from 1% (w/v) polymer solutions in deionized water in flat polytetrafluoroethylene moulds. After evaporation of solvent, the cast films were dried under vacuum at room temperature until constant weight was reached.

Doping procedure

Chemical doping was performed by exposure of polymer films to I_2 or BF_3 vapour. The doping system is shown schematically in *Figure 1*.

Measurements

I.r. spectra of the samples were taken with Nicolet DX510 Fourier transform infra-red (*FT*i.r.) spectrometer. Samples were prepared as thin films or as pellets in KBr. For thermal analysis, a Perkin-Elmer DSC-7 differential scanning calorimeter d.s.c. was used. Conductivity measurements were carried out using standard two-probe and/or four probe techniques.

---

* To whom correspondence should be addressed

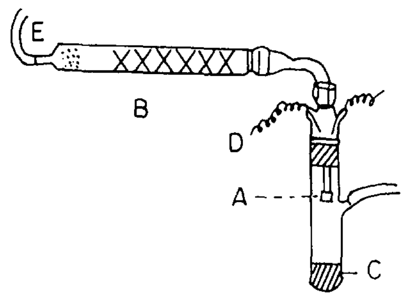


Figure 1 Doping apparatus. (A) Film attached to the wires; (B) P_2O_5 containing tube; (C) I_2 or BF_3-etherate; (D) connection to the two-probe; (E) N_2 inlet

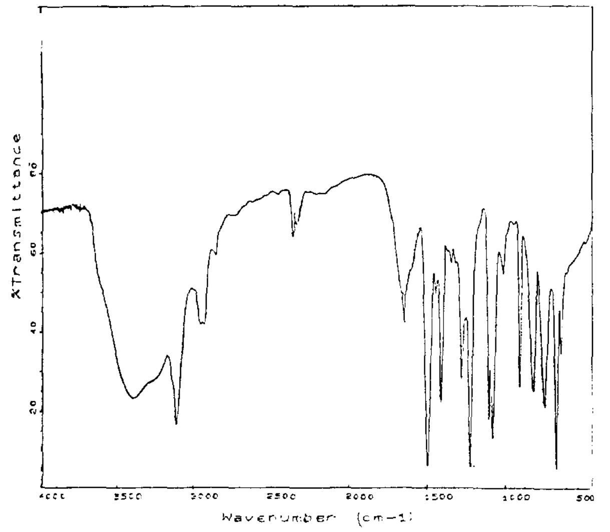


Figure 2 *FT*i.r. spectrum of PVI sample

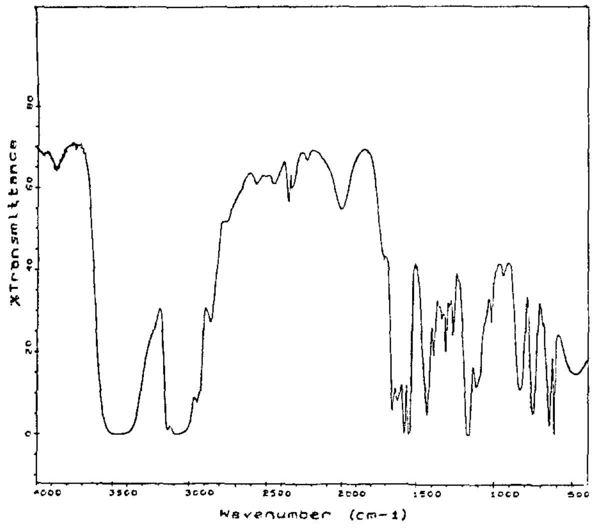


Figure 3 *FT*i.r. spectrum of QPVI sample

Quaternization of PVI

Quaternization was carried out in dimethylformamide solution with methyl iodide under nitrogen atmosphere. Reaction was started at 0°C, then was allowed to warm up to room temperature. The quaternized polymer was recovered by precipitation in acetone and dried at 50°C under vacuum in the form of a pale yellow water-soluble powder.

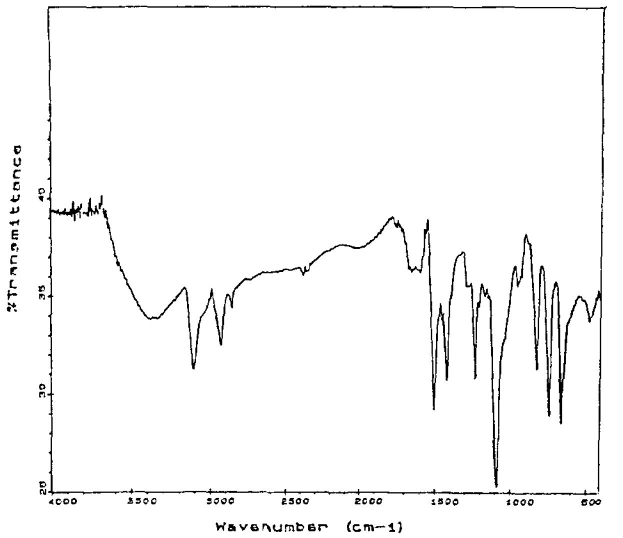
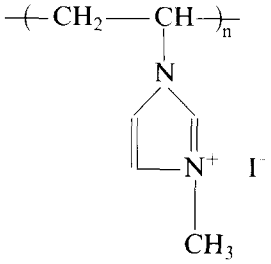


Figure 4 *FT*i.r. spectrum of I_2-doped PVI

RESULTS AND DISCUSSION

From the increase in the weight of PVI sample, percent quaternization was calculated as 87%. The structure of quaternized PVI (QPVI) is given as:



Poly(1-methyl-3-vinylimidazoliniumiodide)

Both quaternized and unquaternized PVI were doped with I_2 and BF_3. Samples were characterized with *FT*i.r. and d.s.c.

*FT*i.r. spectra are shown in *Figures 2–4*. The spectrum of PVI exhibits the peaks as described by Perchard *et al.*[10]. The peaks at 1500, 915 and 820 cm^{-1} are stretching bands assigned to imidazole ring. After quaternization a shift occurs, from 1500 to 1550 cm^{-1} and a band at 1580 cm^{-1} corresponding to the quaternized imidazole ring and two bands at 1690 and 2020 cm^{-1} assigned to the C=N group appear. Furthermore, the bands at 915 and 820 cm^{-1} disappear (*Figure 3*).

The spectra of iodine-doped PVI are shown in *Figure 4*. The bands at 1290 and 915 cm^{-1} corresponding to bending and stretching vibrations of C-H and C-N in the ring disappear.

The conductivity of PVI sample as measured by two-probe technique is less than 10^{-10} S cm^{-1}. It is practically an electrical insulator. After quaternization the conductivity increased to 6.3×10^{-10} S cm^{-1}. The Cu(II) complex of PVI was prepared to investigate the solution properties[11]. The conductivity of a film cast from an aqueous solution of Cu(II)-PVI was tested and found a slightly increased conductivity (1.1×10^{-9} S cm^{-1}) compared to the PVI sample.

To increase the conductivity further, doping with I_2 and BF_3 in vapour was carried out. *Figure 5* shows the

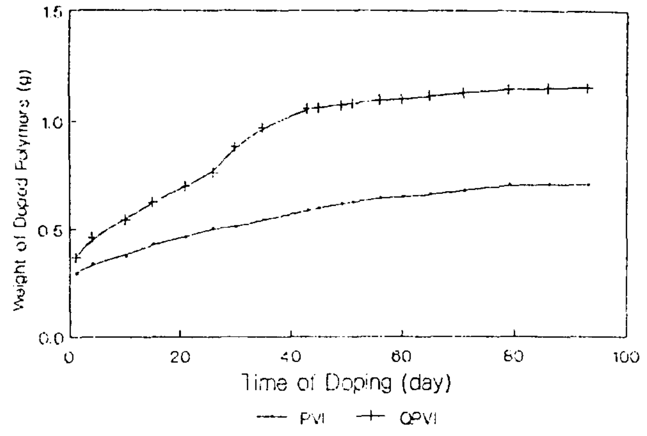


Figure 5 Weight change during I_2 doping on PVI and QPVI

Table 1 Elemental analysis of PVI samples

	Calculated			Experimental		
Sample	%N	%C	%H	%N	%C	%H
PVI	29.8	63.8	6.4	26.5	60.8	6.4
QPVI (87% quaternized)	12.9	32.4	4.0	11.0	31.0	4.8
QPVI (doped with 68.55% I_2)	4.1	10.2	1.3	5.5	10.1	2.0

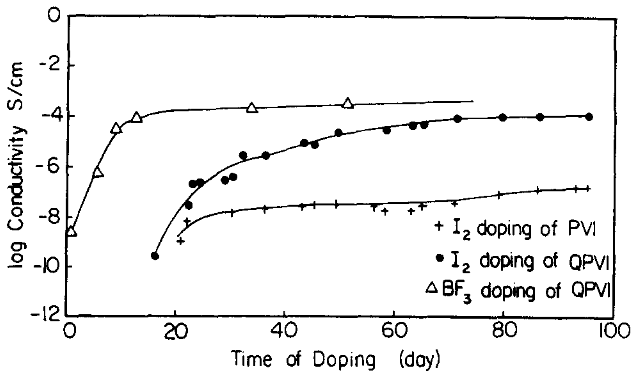


Figure 6 Electrical conductivity *versus* exposure time for I_2-doping and BF_3-doping

Table 2 Glass transition temperatures of PVI samples

Sample	T_g (K)
PVI	373
QPVI	354
Cu(II)-PVI	380
PVI doped with I_2	375
QPVI doped with BF_3	Flexible at room temp.
QPVI doped with I_2	Flexible at room temp.

increase of weight due to iodine intake as a function of time for PVI and QPVI. QPVI can take more iodine into its structure compared to PVI, because the quaternized polymer, as an iodide salt, can react with I_2 to form I_3^-.

Table 1 shows the results of elemental analysis of PVI before and after quaternization and after iodine doping. There are some small differences between calculated and experimental values of C, N and H percentages. *FT*i.r. spectra show that the samples are hygroscopic. Therefore low C, N and high H figures can be due to water absorption.

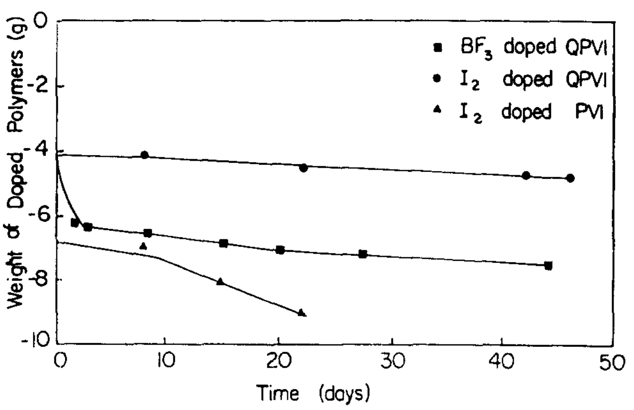


Figure 7 The change of electrical conductivity with time in open atmosphere

Doped samples of PVI and QPVI were not soluble in solvents. Insolubility of doped samples can be attributed to the formation of ionic crosslinks within the polymer network. The following reactions are assumed between polyvinylimidazole and iodine:

$$\text{PVI} + I_2 \rightarrow (\text{PVI})I_2 \qquad \text{outer complex}$$

$$(\text{PVI})I_2 \rightarrow [(\text{PVI})I]^+ + I^-$$

$$[(\text{PVI})I]^+ + I^- + (\text{PVI})I_2 \rightarrow I_3^- + [(\text{PVI})_2I]^+ \qquad \text{inner complex}$$

It is supposed that PVI can form the same type of charge transfer complex with iodine, having a structure like polyvinylpyridine[12].

Figure 6 shows the conductivity change of PVI and QPVI as a function of time of doping. Conductivity increases with increasing dopant concentration and reaches a plateau. The maximum conductivity achieved is 10^{-7} S cm^{-1} for I_2-doped PVI with a mole ratio of I_2/(vinylimidazole unit, VI) of 0.6 and 10^{-4} S cm^{-1} for doped QPVI with a I_2/VI mole ratio of 2.0. This behaviour is different from polyvinylpyridine doped with iodine, in which case[5] the maximum conductivity was reached for a sample with I_2/pyridine mole ratio of 1.5. The conductivity also decreases at both higher and lower levels of iodine in some similar I_2/pyridine systems[13,14].

In BF_3-doping of QPVI, the rise in conductivity from 10^{-9} S cm^{-1} to 1×10^{-5} S cm^{-1} was achieved. BF_3-doping needs less time to reach the plateau, compared to I_2 doping (*Figure 6*).

Results of glass transition temperature (T_g) measurements are given in *Table 2*. Complexation with Cu metal and doping increases the T_g of PVI. These processes create crosslink centres and shift the segmental motion of samples to higher temperatures. The reactions mentioned above explain how iodine works to form crosslinking between PVI chains.

QPVI doped with I_2 or BF_3 was flexible at room temperature. Apparently, these dopants act as plastifying agent. Similar behaviour was observed for polyvinylpyridine doped with iodine[13].

The conductivity of doped samples after exposure to open atmosphere was followed for about two months, as shown in *Figure 7*. Conductivity decreases from 10^{-7} S cm^{-1} to a value less than 10^{-10} S cm^{-1} in 22 days for I_2-doped PVI. For BF_3-doped QPVI samples, conductivity decreases from 10^{-4} to 10^{-6} S cm^{-1} in a

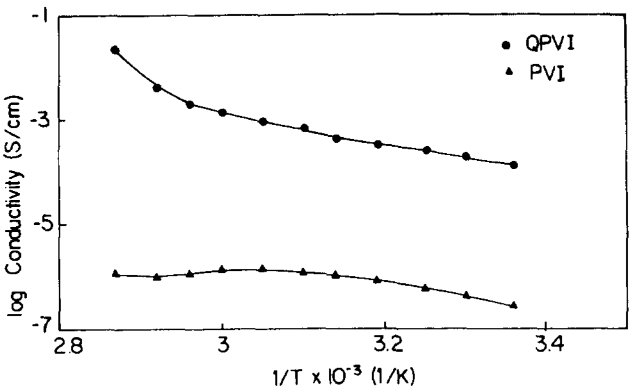


Figure 8 Arrhenius plot for the electrical conductivity

few days. The change in conductivities presumably results from the destruction of charge transfer complexes in open atmosphere. Conductivities of I_2-doped QPVI samples do not change very much in open atmosphere. Conductivity reduced only by one order of magnitude in about 50 days. This result indicates that bonding of iodine to QPVI is stronger, as compared to bonding to unquaternized PVI.

The temperature dependence of ionic conductivity (σ) for I_2-doped PVI and QPVI was examined, and found to fit the Arrhenius equation.

$$\sigma = A\exp(-E/RT)$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the temperature (*Figure 8*). By a 50 K increase in temperature above room temperature, the conductivity of I_2-doped QPVI increased from 10^{-4} to $10^{-2}\,\mathrm{S\,cm^{-1}}$, and that of PVI from 10^{-7} to $10^{-6}\,\mathrm{S\,cm^{-1}}$. Since QPVI has more charge carriers compared to PVI, the rise in conductivity with temperature is more.

CONCLUSION

Conductive polymer was obtained from poly(N-vinylimidazole) by quaternization and I_2 and BF_3-doping. Conductivity increases with increasing I_2/VI ratio, reaching a plateau value of $10^{-4}\,\mathrm{S\,cm^{-1}}$ for the maximum iodine intake for which the I_2/VI mole ratio is equal to 2.

Iodine-doped QPVI samples are processible. They are flexible at room temperature. Iodine-doped QPVI samples maintain their conductivities for about two months in open atmosphere. Conductivities of doped samples increase with increasing temperature, indicating semiconductor behaviour.

ACKNOWLEDGEMENT

The authors would like to thank the Turkish Scientific and Technical Research Council, for the research grant TBAG-U/15-6.

REFERENCES

1 Skotheim, T. A. (Ed.) 'Handbook of Conducting Polymers', Marcel Dekker, New York, 1986
2 Machado, J. M., Karasz, F. E. and Lenz, R. W. *Polymer* 1988, **29**, 1412
3 Galvin, M. E. and Wnek, G. E. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 2727
4 Nugay, N., Küçükyavuz, Z. and Küçükyavuz, S. *Polymer* 1993, **34**, 4649
5 Nugay, N., Küçükyavuz, Z. and Küçükyavuz, S. *Polymer* 1994, **35**, 243
6 Henrichs, P. M., Whitlock, L. R., Sochor, A. R. and Tan, J. S. *Macromolecules* 1980, **13**, 1375
7 Tan, J. S. and Sochor, A. R. *Macromolecules* 1981, **14**, 1700
8 Overberger, C. G., Smith, T. W. and Dixon, K. W. *J. Polym. Sci., Polym. Symp.* 1975, **50**, 1
9 Overberger, C. G. and Smith, T. W. *Macromolecules* 1975, **8**, 401
10 Perchard, C., Bellocq, H. A. and Novak, A. *C. Chim. Phys. Chim. Biol.* 1965, **62**, 1344
11 Abbasnejad, N., M.Sc. Thesis, METU, Ankara, 1992
12 Stankovic, R. H., Lenz, R. W. and Karasz, F. *Eur. Polym. J.* 1990, **26**, 675
13 Möller, M. and Lenz, R. W. *Makromol. Chem.* 1989, **190**, 1153
14 Philips, G. M. and Unterecker, D. F. *Proc. Electrochem. Soc.* 1980, **80**, 195