Polymer Bulletin 33, 325–329 (1994)

Polymer Bulletin

# Layered poly(naphthalene) films prepared by electrochemical polymerization

**Gaoquan Shi*, Gi Xue, Cun Li, and Shi Jin**

Department of Polymer Science and Engineering, Nanjing University, Nanjing 210008, Peoples Republic of China

## SUMMARY

Poly(naphthalene) (PN) has been deposited on a platinum electrode by direct oxidation of naphthalene in $BF_3$-ethyl ether solution containing $5x10^{-3}$ mol/l water. Experimental results demonstrated that the PN films obtained from the described medium composed many parallel arranged polymer layers. The structures, conductivities and heat resistant properties of the PN products were also studied.

## INTRODUCTION

Electrochemical polymerization is a useful method for producing aromatic conductive polymers such as poly(pyrrole)<sup>1)</sup>, poly(thiophene)<sup>2)</sup>, poly(benzene)<sup>3)</sup>, poly(selenophene)<sup>4)</sup> and poly(pyridazine)<sup>5)</sup>, etc. However, only a few publications concerned the electrochemical polymerization of naphthalene, and almost all of them reported polymerization using copper(I) chloride composite as electrolyte<sup>6,7)</sup>. Furthermore, the PNs obtained from these systems were powder-like. Recently, we found $BF_3$-ethyl ether solution containing a controlled amount of water was a good solvent and a good electrolyte for the electrochemical polymerization of naphthalene, and could conveniently get PN films. The PN films formed in this medium composed many parallel arranged polymer layers.

---

*Corresponding author

## EXPERIMENTAL

### Materials

Analytical grade naphthalene, $BF_3$-ethyl ether solution, benzene, ethyl ether and alcohol were purchased from Shanghai 2nd Chem. Co. Naphthalene had been recrystallized from alcohol before using. PN films were purified by washing with distilled ethyl ether, and then dried at 110°C under vacuum for 24 h. The purified product was immersed into benzene (1 g PN in 50 ml benzene) and stirred for 30 min, then the soluble part was separated from insoluble part by centrifugalization. Both polymer components were well dried for characterizations.

### Equipments and Methods

The electrochemical cell consisted of a classical three-electrode connected to a PARC M273 poteniostat. All the solutions were deaerated by a dry argon stream and maintained a light over-pressure during the experiments. The working and counter electrodes were separated from each other by a sintered glass disk, which was made according to a published procedure[8)]. The distance between these 2 electrodes was about 0.5 cm, and each of the electrodes was 99.9% platinum sheet and had a size of 5x0.5 (cm). The reference electrode was Ag/AgCl. The molar mass of soluble PN was measured by a vapor pressure osmometer made by Knauer Co. Infrared spectra were taken out on a Nicolet 170SX spectrometer. Decomposition temperatures were measured by using a thermal analysis balance model WRT-2(Shanghai). Scanning electron microscopy picture was taken out by using an X560 electron micrographer. *dc* conductivities were measured by using the conventional four-electrode method.

## RESULTS AND DISCUSSION

An amount of 0.15 g naphthalene dissolved into 30 ml $BF_3$-ethyl ether solution containing $5\times10^{-3}$ mol/l water which reserved in a plastic compartment, and 1.5 V potential was applied for electrolysis. In a few seconds, the surface of the working electrode changed into red and then gradually changed into black. These phenomena implied the formation of PN and the change in its doping extent. Undoped PN is red in color, and deep doped PN is black[6)]. The purified product was partly soluble in benzene, toluene and acetone, etc. The content of the soluble part in the product was variable with applied potentials. When the applied potential was as low as 1.0 V, almost only soluble polymer was obtained. When the applied potential was as high as 2.5 V, nearly only insoluble polymer was obtained.

**Table I.** Soluble polymer content in the products produced at various applied potentials.

| Applied Potential (V) | Soluble Polymer Content (wt%) |
|---|---|
| 1.0 | 95 |
| 1.2 | 92 |
| 1.5 | 80 |
| 2.0 | 42 |
| 2.5 | 6 |

The molar mass of the soluble polymer was measured to be 4600 g/mol, and the number of repeat units was about 37. Elemental analysis results showed its C:H ratio was 10:6.02, very close to the theoretical value for disubstitued chain. On the other hand, the C:H ratio of the insoluble polymer was 10:5.67, a little higher than 10:6. The visible spectrum bands of soluble polymer in acetone were appeared at 530 nm, 490 nm, and 460 nm. The IR spectra of both soluble and insoluble polymers are shown in Figure 1. The 760 $cm^{-1}$ and 840 $cm^{-1}$ in the spectrum of soluble polymer can be attributed to the out-of-plane stretching of 1,4-poly(naphthalene). The relative intensities of these two bands are similar to that for chemically synthesized 1,4-poly(naphthalene)[9]. The IR band of insoluble polymer are broader than those appeared in the spectrum of

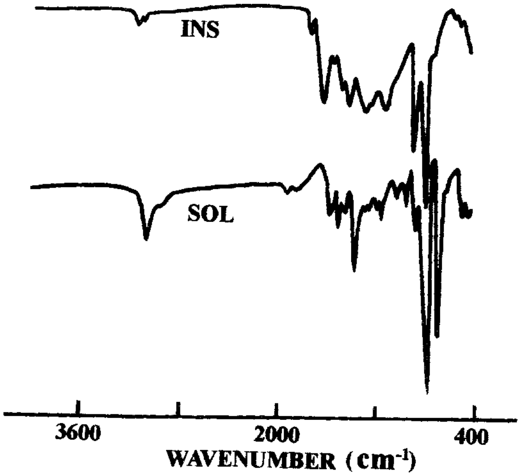

**Figure 1.** The IR spectra of soluble (SOL) and insoluble(INS) PNs.

soluble polymer. Furthermore, the 760 cm$^{-1}$ band assigned to the out-of-plane vibration of the 4 adjacent hydrogen of 1,4-poly(naphthalene) which appeared in the spectrum of soluble polymer, however, was very weak in this spectrum. On the basis of elemental analysis and IR results described above, it is reasonable to conclude that the insoluble polymer is 1,4-poly(naphthalene) with crosslinking.

The PN film deposited on Pt composed many polymer layers as shown in its scanning electron microscopy (Fig.2). The polymer layers were parallel to the electrode surface and the outside layers were destroyed by washing with ethyl ether. The original PN film peeled from the electrode was a semiconductor. Its conductivity in the direction parallel to the film surface was about 2.5x10$^{-3}$ Scm$^{-1}$. However, in the film thickness direction, its conductivity was only 1.48x10$^{-5}$ Scm$^{-1}$. These findings also supported the results showed by SEM. Since the soluble and insoluble PNs obtained from the original PN films are powders, their conductivities were measured by using their pressed pallets as samples. The conductivity of the soluble polymer was 1.2x10$^{-3}$ Scm$^{-1}$, and that of insoluble polymer was 1.5x10$^{-6}$ Scm$^{-1}$.

**Figure 2.** SEM picture of the PN film deposited on a platinum electrode surface. S=7.5 µm.

Figure 3 illustrates the TG curves of soluble and insoluble PNs. As seen from this figure, each curve has a little weight loss in the temperature range of 150-200 °C, mainly due to the evaporation of low molecular components such as PN oligomers, solvents and naphthalene monomer. The decomposition of soluble polymer started at 457 °C, and weight losing fast. On the other hand, the decomposition of insoluble polymer was taken placed at the temperature above 588 °C, and weight losing slowly. These results implied that the crosslinking of the polymer chains improved its heat-resistant property, despite decreased its conductivity.

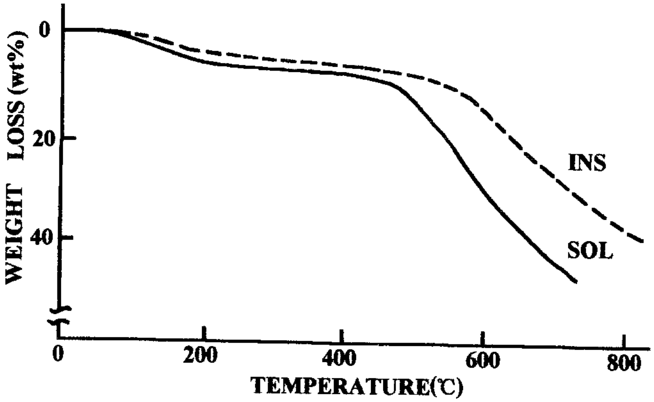

**Figure** 3. TG diagrams of soluble (SOL) and insoluble (INS) PN products.

REFERENCES

1) A. F. Diaz, K. K. Kanazawa, C. P. Cardini, J. Chem. Soc., Chem. Commun. 653(1979)
2) V. L. Afanas'ev, I. B. Nazaraova, M. L. Khidekel, Izv. Akad. Kauk SSSR, Ser. Khim. 1687(1980)
3) L. M. Goldenberg, S. Aeiyach, P. C. Lacaze, J. Electroanal. Chem. 335, 151(1992)
4) K. Yoshino, Y. Kohono, T. Shiraushi, K. Kaneto, Synth. Met. 10, 319(1985)
5) M. Satoh, K. Kaneto, K. Yoshino, J. Chem. Soc., Chem. Commun. 1627(1984)
6) M. Satoh, F. Uesugi, M. Tabata, K. Kaneto, K. Yoshino, J. Chem. Soc., Chem. Commun. 550(1986)
7) S. Hara, N. Tashima, Chem. Lett. 269(1990)
8) M. Sato, K. Kaeriyama, K. Aomeno, Makromol. Chem., 184, 2241(1983)
9) S. Aeiyach, C. Dobois, P. C. Lacaze, J. Chem. Soc., Chem. Commun. 1608(1986)

Accepted June 13, 1994 Shi