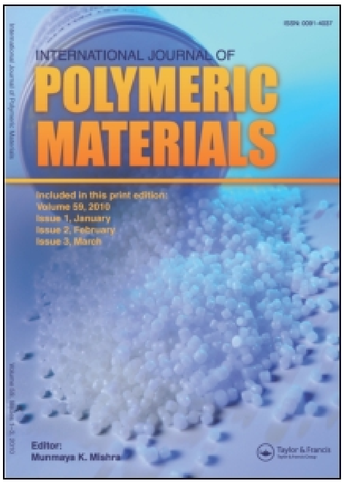


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

ELECTROCHEMICAL POLYMERIZATION OF NAPHTHOLS IN AQUEOUS MEDIUM

M. Y. Abdelaal[a][b]
[a] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt [b] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, ET, Egypt

To cite this Article Abdelaal, M. Y.(2005) 'ELECTROCHEMICAL POLYMERIZATION OF NAPHTHOLS IN AQUEOUS MEDIUM', International Journal of Polymeric Materials, 54: 3, 151 — 159
To link to this Article: DOI: 10.1080/00914030390207237
URL: http://dx.doi.org/10.1080/00914030390207237

International Journal of Polymeric Materials, 54:151–159, 2005

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390207237

ELECTROCHEMICAL POLYMERIZATION OF NAPHTHOLS IN AQUEOUS MEDIUM

M. Y. Abdelaal
Chemistry Department, Faculty of Science, Mansoura University,
Mansoura, Egypt

In this work poly(1-naphthol) and poly(2-naphthol), designated as poly(NAP-1) and poly(NAP-2), respectively, have been electrochemically synthesized. The electrochemical synthesis was achieved by using aqueous solution of sodium hydroxide as an electrolyte. The chemical structure of the formed polymers was proved by means of ex-situ FT-IR spectroscopy and compared with those previously prepared in non-aqueous solutions. The electrochemical polymerization mechanism was discussed.

Keywords: naphthol, electrochemical polymerization, FT-IR

INTRODUCTION

Conducting polymers have attract much interest during the previous few decades. Polymer-coated electrodes have several attractive features in biosensor production, one of which is the convenience of immobilizing reagents near the electrode surface in high concentration while preventing interface creation and electrode fouling. An electrochemically generated layer of poly(o-aminophenol) has been used as polymeric coating for the construction of an amperometric hydrogen peroxide biosensor [1].

The ability of 1-naphthol **(1)** to form conducting polymers by anodic polymerization in non-aqueous media is unique [2−5]. In spite of their interesting properties, poly(naphthol)s have received attention less than other conducting polymers such as polyanilines [6−9], polypyrroles [10−13], and polythiophenes [14−17]. Copolymerization is effective for modification and control of the physico-chemical

Received 19 February 2003; in final form 26 February 2003.

Address correspondence to Dr. Magdy Y. Abdelaal, Chemistry Department, Faculty of Science, Mansoura University, Mansoura ET-35516, Egypt. E-mail: magdyabdelaal@yahoo.com

properties of the conducting polymers [18–26]. Polymerization of phenols yields usually thin insulating films [27–32].

It has been reported that electrochemical oxidation of **(1)** in acetonitrile leads to the formation of a conducting and an electroactive polymer film of poly(1-naphthol) containing alternating naphthalene and furan rings [4,5]. From the previously reported results, it could be concluded that the conductivity of such a polymer film [5] may be due to the alternating naphthalene and furan rings, instead of the poly(naphthalene oxide) obtained in the alkaline methanolic solution, which has no furan rings along the polymeric backbone [33]. On the other hand, the electrochemical oxidation of 2-naphthol (17) in acetonitrile leads to the formation of a less conducting polymer film of poly(2-naphthol) [32]. In the present work, poly(1-naphthol) **(P2)** and poly(2-naphthol) **(P4)** denoted as Poly(NAP-1) and Poly(NAP-2), respectively, were prepared by electrochemical oxidation of **(1)** and **(17)**, respectively, from a bath containing an aqueous solution of sodium hydroxide.

RESULTS AND DISCUSSION

The use of sodium hydroxide is more advantageous than the nonaqueous medium used in the reported work [5]. It facilitates dissolution of naphthols and acts as an electrolyte, instead of perchlorate or hexafluoroarsinate salts, without any precautions against humidity, in addition to its feasibility from an economic point of view. The obtained polymeric material was initially deposited on the electrode, and then with continued electrolysis it fell off into the solution. The polymer structure and the electropolymerization mechanism were confirmed by using the *ex-situ FT-IR*-spectroscopic analysis and elemental analysis.

Structure of Poly(1-naphthol) (P2)

The *ex-situ FT-IR* spectroscopic analysis in Figure 1 showed all the bands related to the polymer structure [34]. For furan rings, the corresponding absorption of C=C stretching at 1570 cm^{-1} was observed in addition to other two absorptions at 1080 cm^{-1} with shoulder at 1060 cm^{-1} for symmetric vibrations and at 1290 cm^{-1} for the asymmetric vibrations of C–O–C bond. For naphthalene rings, $C=C_{ar}$ stretching band is observed at 1590 cm^{-1} and C–C stretching between monomeric moieties at 1124 cm^{-1} is also detected. It also showed the presence of naphthol groups at the chain ends of the polymer as indicated by OH stretching at

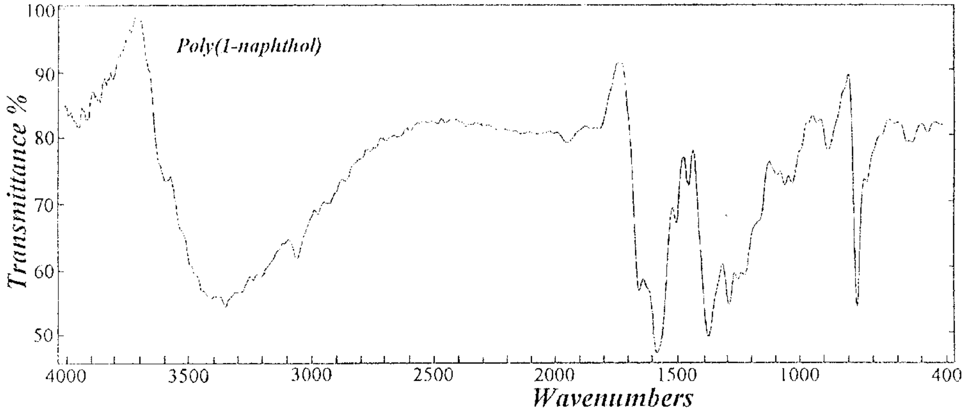


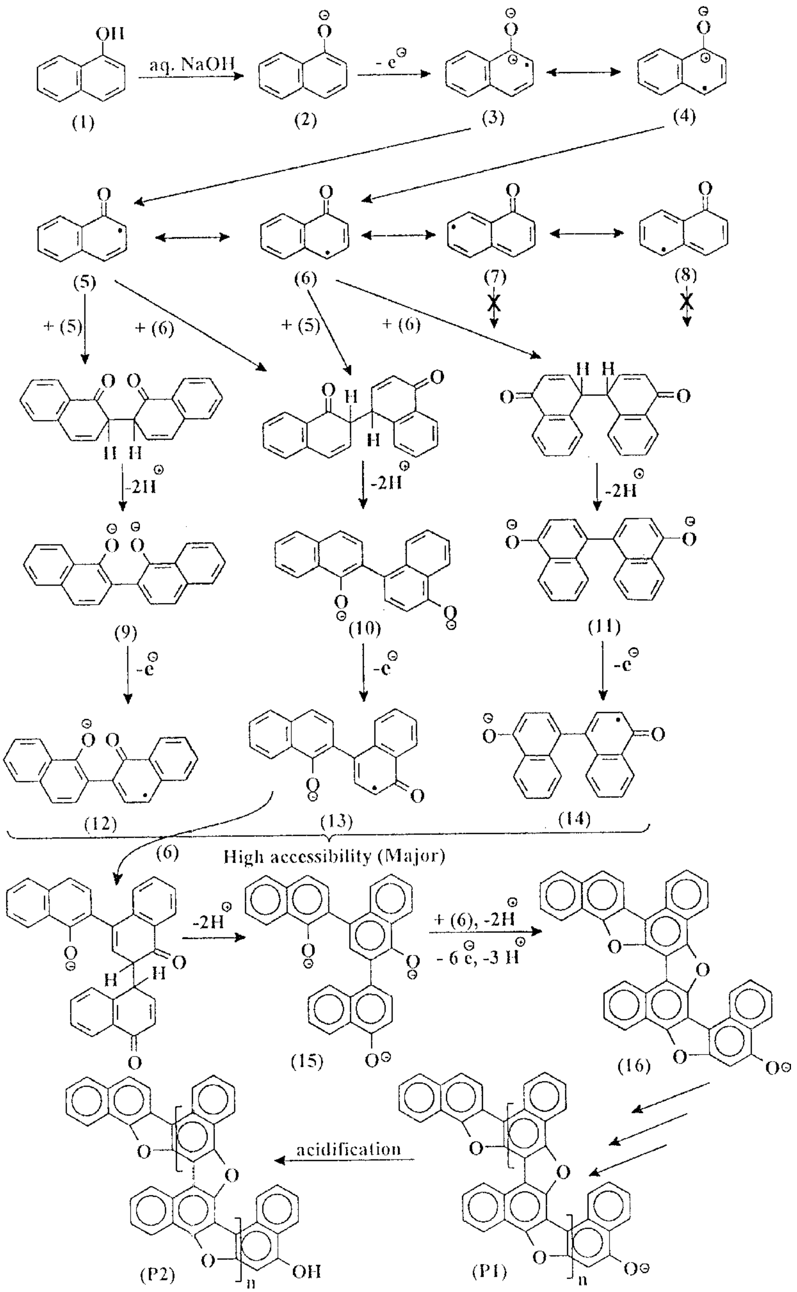
FIGURE 1 *FT-IR* spectrum of poly(1-naphthol) **(P2)** in the solid state using KBr wafer.

~3500 cm^{-1} as well as the absorption at 1665 cm^{-1} for the quinone groups. The C–H vibrations of the four adjacent H-atoms are situated at 765 cm^{-1}. Also, there is no absorption neither at 815 cm^{-1} for 2-adjacent H-atoms nor at 750 cm^{-1} and/or 800 cm^{-1} for 3-adjacent H-atoms. This means that the second nucleous of naphthalene is not participating in the polymerization mechanism. Also, elemental analysis proves the empirical formula of the obtained polymer as $(C_{10}O)_n$. The presence of electronic conducting layers is expected and indicated by increasing the absorption in the domain of 2000–4000 cm^{-1} as concluded and reported before [35].

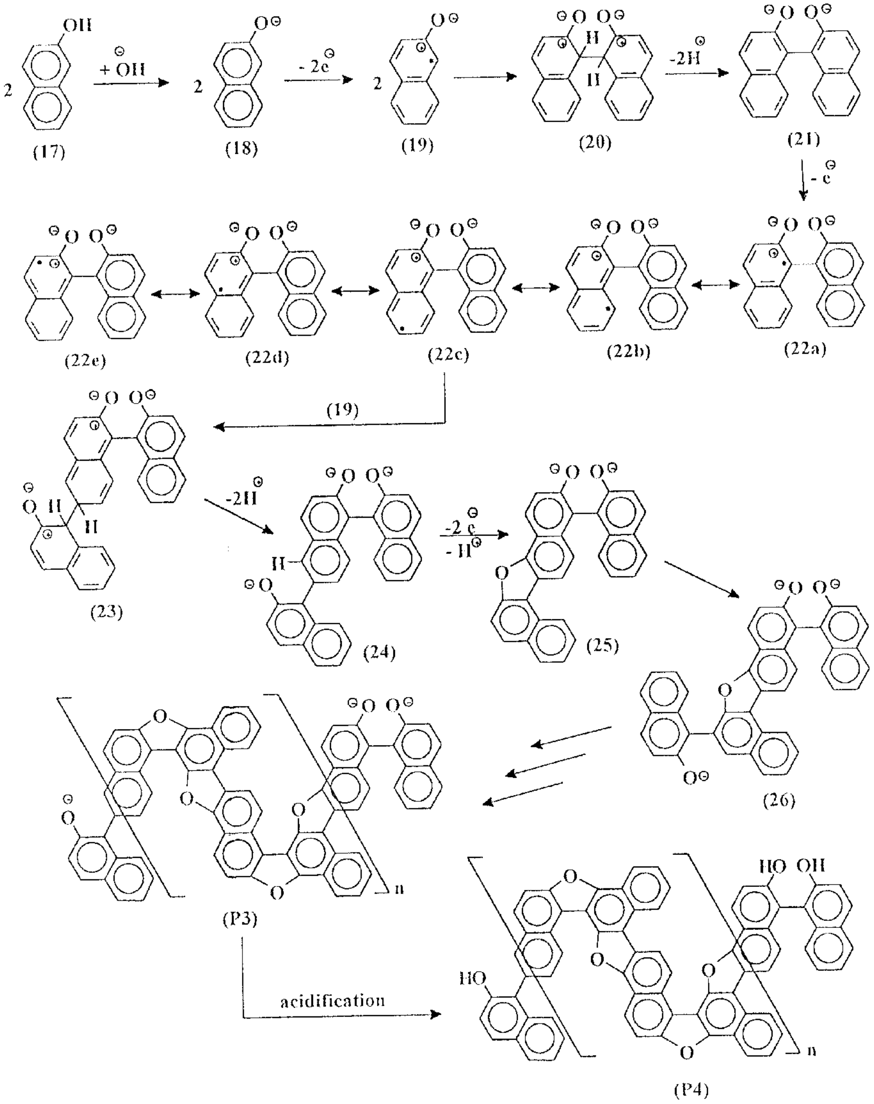
Polymerization Mechanism of 1-naphthol(1)

A polymerization mechanism for **(1)** in an aqueous medium can be suggested in parallel to that previously reported for the non-aqueous medium and in presence of perchlorate or hexafluoroarsinate salts as electrolyte [5]. Scheme 1 represents the suggested mechanism for the electropolymerization of **(1)**.

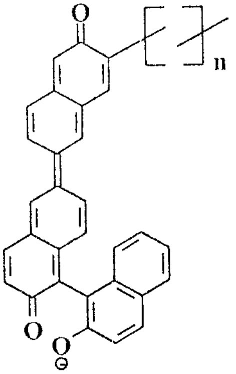
The use of aqueous sodium hydroxide solution lead to dissociation of **(1)** into its conjugate base **(2)**. This facilitates the formation of the radical-cation **(3)** and stabilizes it through resonance with the radical-cation **(4)**. The propagation reaction can be achieved through the most probable o–p′ coupling for dimer radical **(13)** while it may involve either p–o′ or o–p′ coupling for dimer radicals **(12)** and **(14)**, respectively. Both of them are expected to produce similar products. This means that, in all cases, the propagation reaction is expected to take place through the reaction at the o-position of the attacking monomer radical and will be continued from the p-position or vice versa leading to the same polymer structure except in the beginning of the polymer chains. On the other hand, the radical ketones **(7)** & **(8)** are not involved in the electrochemical oxidation as the *ex-situ FT-IR* spectrum is free from absorption either at $\nu = 815$ cm^{-1} for C–H out-of-plane vibrations of 2-adjacent hydrogen atoms or at $\nu = 750$ and/or 800 cm^{-1} for C–H out-of-plane vibrations of 3-adjacent hydrogen atoms. Concurrently with these reactions, the nucleophilic reaction of the phenoxide oxygen leads to cyclization and formation of polymer chains containing furan rings in an alternating manner with the naphthalene rings **(P1)**. Cyclization reaction may be facilitated by the presence of aqueous sodium hydroxide. Acidification renders the obtained polymer **(P1)** into the associated form **(P2)**.



SCHEME 1 The mechanism of the electrochemical polymerization of 1-naphthol(**1**).



SCHEME 2 The mechanism of the electrochemical polymerization of 2-naphthol(**17**).



(P5)

SCHEME 2 Continued.

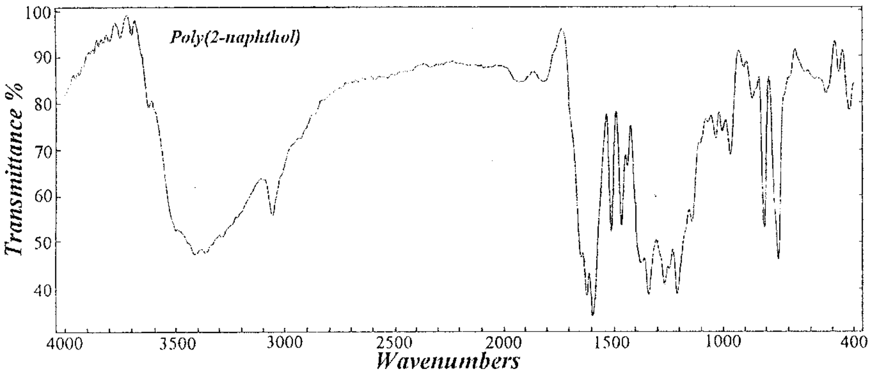


FIGURE 2 *FT-IR* spectrum of poly(2-naphthol) **(P4)** in the solid state using KBr wafer.

Structure and Polymerization Mechanism of Poly(2-naphthol) (P4)

The *Ex-situ FT-IR* spectroscopic analysis of poly(2-naphthol) **(P4)** in Figure 2 showed absorbencies similar to those obtained by poly(1-naphthol) **(P2)** synthesized under the same conditions. This indicates that the obtained polymer consists also of alternating naphthalene and furan rings. Moreover, a new band at 815 cm^{-1} related to two aromatic adjacent hydrogen atoms [34] is detected as intense as the 759 cm^{-1} band. This indicates that the second nucleus intervenes in the electrochemical polymerization mechanism of **(17)** represented in Scheme 2, parallel to that previously proposed and verified one [32].

The radical-cations (**22a,b,d,** and **c**) are excludes on the bases of steric hindrance and on the basis of *FT-IR* spectrum of the obtained polymer. *FT-IR* spectrum confirms the intervening of the second nucleus in the electrochemical polymerization and only the radical-cation **(22c)** is expected to complete the polymerization of **(17)**. The absorption increases also in the 2000–4000 cm^{-1} domain indicating the presence of electronic conducting layers as concluded and reported before [35].

Moreover, the spectra of both polymers **(P2)** and **(P4)** have an intense band at 1660 cm^{-1} corresponding to the carbonyl group formed by oxidation of the chain ends into the quinonoid form **(P5)**.

EXPERIMENTAL

All materials were supplied by Aldrich, Milwaukee, WI, USA and were used without further purification. Poly(1-naphthol) **(P2)** and poly(2-naphthol) **(P4)** have been prepared by using a single compartment electropolymerization bath containing 1 g (7 mmol) of 1-naphthol **(1)** or 2-naphthol **(17)** dissolved in 100 ml aqueous solution of 0.1 M NaOH.

Electrolysis was carried out using a constant power dc source (VIZ, model WP-704AX). A electric voltage of 4.0 V was applied under stirring conditions between two platinum sheets of 3.0 cm^2 surface area for 4 h. The obtained polymers were initially deposited on the electrode and with continued electrolysis, they fell off into the solution. They were filtered off, washed thoroughly with distilled water and converted into the H-form by neutralization with the aid of HCL. *Ex-situ FT-IR* spectra were recorded on a Mattson 5000 FT-IR spectrometer.

Elemental analysis has been performed by using Perkin Elmer 2400 Series II CHNS/O analyzer. Elemental analysis ($C_{10}H_4O$): Found (Calcd.): C, 85.50 (85.71); H, 3.11 (2.88); O, 11.39(11.42).

REFERENCES

[1] M. A. V. Garcia, P. T. Blanco, and A. Ivaska, *Electrochimica Acta* **43**(23), 3533 (1998).
[2] M. C. Pham, J. Moslih, C. Barbero, and O. Haas, *J. Electroanal. Chem.* **316**, 437 (1991).
[3] H. A. Abd-El-Rahman, *Thin Solid Films* **310**, 208 (1997).
[4] M. C. Pham, J. Moslih, and P. C. Lacaze, *J. Electroanal. Chem.* **278**, 415 (1990).
[5] M. C. Pham, J. Moslih, and P. C. Lacaze, *J. Electrochem. Soc.* **138**, 449 (1991).
[6] H. A. Abd El-Rahman, *Polym. Int.* **44**, 481 (1997).
[7] G. Inzelt and V. Kertesz, *Electrochim. Acta* **42**, 229 (1997).
[8] L. T. Cai and H. Y. Chen, *J. Appl. Electrochem.* **28**, 161 (1998).

[9] K. H. Lubert and L. Dunsch, *Electrochim. Acta* **43**, 813 (1998).

[10] T. Tatsuma, T. Sotomura, T. Sato, D. A. Buttry, and N. Oyama, (1995). *J. Electrochem Soc.* **142**, L182.

[11] C. A. Ferreira, S. Aeiyach, J. J. Aaron, and P. C. Lacaze, *Electrochim. Acta* **41**, 1809 (1996).

[12] C. E. Ehrenbeck and K. Juettner, *Electrochim. Acta* **41**, 1815 (1996).

[13] H. Eisazadeh, A. A. Rostami, and H. Nikooford, *Iran J. Polym. Technol.* **10**, 167 (1997).

[14] H. L. Bandey, P. Gremis, S. E. Garner, A. R. Hillman, J. B. Raynor, and A. D. Workman, *J. Electrochem. Soc.* **142**, 2111 (1995).

[15] U. Barsch and F. Beck, *Electrochim Acta* **41**, 1761 (1996).

[16] J. R. Reynolds, G. A. Sotzing, C. A. Thomas, and D. J. Trvin, *Polym. Prepr.* **39**, 83 (1998).

[17] T. W. Smith, D. J. Luca, S. Kaplan, and M. A. Abkowitz, *Polym. Prepr.* **39**, 58 (1998).

[18] H. H. Rehan, *Polymer Inter.* **49**, 645 (2000).

[19] Y. Wen, R. Harniharan, and S. Patel, *Macromolecules* **23**, 758 (1990).

[20] S. K. Dhawan and D. C. Trivedi, *Synth. Met.* **60**, 63 (1993).

[21] J. A. Conklin, S. C. Huang, S. M. Huang, T. Wen, and R. B. Kaner, *Macromolecules* **28**, 6522 (1995).

[22] H. Tsutsumi, S. Fukuzawa, M. Ishikawa, M. Morita, and Y. Matsuda, *J. Electrochem. Soc.* **142**, L168 (1995).

[23] S. Ye, F. Girard, and D. Belanger, *J. Phys. Chem.* **97**, 12373.

[24] S. Ye, S. Besner, L. H. Dao, and A. K. Vijh, (1995) *J. Electroanal. Chem.* **381**, 71 (1993).

[25] C. Carelli, I. Chairotto, A. Curulli, and G. Palleschi, *Electrochim. Acta* **41**, 1793 (1996).

[26] H. Tanaka, H. Katsuura, and S. Torii, *Electrochim. Acta* **42**, 2019 (1997).

[27] F. Bruno, M. C. Pham, and J. E. Dubois, *Electrochim. Acta* **22**, 451 (1997).

[28] M. C. Pham, P. C. Lacaze, and J. E. Dubois, *J. Electroanal. Chem.* **86**, 147 (1978); **99**, 331 (1979); **117**, 233 (1981).

[29] Y. Ohunki, T. Ohsaka, II. Matsuda, and N. Oyama, *J. Electroanal. Chem.* **158**, 55 (1983).

[30] M. C. Pham, A. Hachemi, and M. Delamer, *J. Electroanal. Chem.* **199**, 153 (1985).

[31] R. L. McLarely, R. E. Thomas, E. A. Arene, and R. W. Murray, *J. Electroanal. Chem.* **290**, 79 (1990).

[32] M. C. Pham, J. Moslih, and P. C. Lacaze, *J. Electroanal. Chem.* **303**, 297 (1991).

[33] M. C. Pham, A. Hachemi, and M. Delmar, *J. Electroanal. Chem.* **134**, 197 (1985).

[34] G. Socrates, *Infrared Characteristic Group Frequencies*, (NY: Wiely), 1980.

[35] G. B. Street, in *Handbook of Conducting Polymers vol. 1*, Ed. T. A. Skotheim (Marcel Dekker, New York, 1986) p. 279ff.