Synthesis and electroactivity of pyrrole end-functionalized poly(2-methyl-2-oxazoline)

A. Cirpan [a], S. Alkan [a], L. Toppare [a,*], G. David [b], Y. Yagci [c,*,1]

[a] *Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey*
[b] *Department of Macromolecules, 'Gh Asashi' Technical University, 6600 Jassy, Romania*
[c] *Department of Chemistry, Istanbul Technical University, Maslak, 80626 Istanbul, Turkey*

Abstract

Poly(2-methyl-2-oxazoline) (PMeOZO) with pyrrole end groups was synthesized by cationic ring polymerization of 2-methyl-2-oxazoline initiated by benzyl bromide and subsequent modification of the halide end group. The structure and electroactivity of the macromonomer thus obtained were confirmed by spectral analysis and cyclic voltametry, respectively. The posssibility of chemical and electrochemical graft copolymerization of PMeOZO with pyrrole was also studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Macromonomer; Pyrrole functionalization; Poly(2-methyl-2-oxazoline)

1. Introduction

Polyethylenimine and their derivatives, especially poly(2-oxazolines), are known as key compounds, opening up new aspects of polymerization chemistry of cyclic iminoethers and materials science. The versatile utilization of the living character of oxazolines polymerization allowed the obtention of sophisticated functional polymers for a large range of applications: nonionic polymer surfactants, stabilizers for preparation of monodisperse particles, polymer networks (including nonionic hydrogels), polymer composites, biorelated materials, optically active materials, thermotropic liquid crystalline polymers, phase-transfer catalysts, detergents, oil dispersants, adhesives, etc. [1,2]. The macromonomer technique is proved to be useful for preparing graft copolymers [3–6]. Macromonomers are, in fact, polymers possessing polymerizable end groups which can copolymerize with low molecular weight monomers. These molecules can be prepared by using functional initiators or by end capping the living growing chains with an appropriate nucleophile or by chemical coupling of telechelic compounds. We have recently described the use of several controlled polymerization methods for preparing pyrrole and thiophene functional macromonomers including atom transfer radical polymerization, cationic ring opening polymerization and anionic polymerization [7, 8]. These macromonomers were subsequently used in the electrocopolymerization with pyrrole or thiophene, depending on the related functionalization, to yield graftcopolymers [9–16]. This way, while the high conductivity originating from the polypyrrole or polythiophene segments is maintained, the processability and mechanical properties were improved by incorporation of the corresponding grafts.

The present article reports on the synthesis and electroactivity poly(2-methyl-2-oxazoline) (PMeOZO) macromonomer with pyrrolyl group.

---

[*] Corresponding authors. Tel.: +90-212-285-6169; fax: +90-212-285-6386.

E-mail address: yusuf@itu.edu.tr (L. Toppare).

[1] Fax: +90-212-2853241.

2. Experimental

2.1. Materials

2-Methyl-2-oxazoline (MeOZO) (Aldrich) and pyrrole (Py) (Aldrich) were freshly distilled under reduced pressure. MeOZO was stored on molecular sieves and pyrrole was kept at 0°C, in the dark, until it was used. Chloroform (Aldrich) was purified by distillation over P_2O_5. Acetonitrile (ACN) (Merck) was vacuum distilled and kept on molecular sieves. Toluene (Aldrich) was purified and dried by conventional method (reflux on natrium wires, distillation, then kept on calcium hydride, distilled). Diethyl ether was distilled over sodium wire. The other reagents, i.e. benzyl bromide (BB) (Aldrich), potassium (Aldrich), tetrabutylammonium iodide (Aldrich), tetrabutylammonium tetrafluoroborate (TBAFB) (Sigma), *p*-toluene sulfonic acid (PTSA) (Sigma), Sodium dodecyl sulfate (SDS) (Sigma) and $FeCl_3$ (Merck) were used as received.

2.2. Macromonomer synthesis

The monofunctional PMeOZO macromonomer was synthesized by the coupling of terminal alkyl bromide groups of the oligomers with pyrrolyl potassium. Attempts to obtain the macromonomer by end capping of the growing living chains with pyrrole or pyrrolyl potassium failed. In the first case, the proton scavenger used – poly(4-vinylpyridine-co-divinylbenzene) copolymer (PyDVB beads with a diameter of about 4 mm), with a content of 10.4% N – was not efficient enough, and the product was quaternized. In the second case, some secondary reactions occurred or gave low molecular products.

Pyrrolyl potassium was obtained by the direct reaction between potassium and pyrrole in toluene under inert atmosphere (argon). In a three necked round bottom flask equipped with an inlet, a dropping funnel and a connecting adapter related with an oil trap, 1.2 g (30 mmol) carefully cleaned potassium were added in small pieces to 30 ml toluene. The system was purged for 15 min with argon, and 3.2 ml (45 mmol) pyrrole in 15 ml dried toluene was dropwise added to the stirred mixture. The temperature was first raised to 70°C for 6 h, and then the system was maintained at reflux for 8 h, at which time all solid particles disappeared. The yellowish liquid was distilled under argon flow. The crude solid product was vacuum dried.

3 g oligomer (1.4 mmol, DP = 23, evaluated from ^{1}H-NMR data), obtained by the cationic polymerization of MeOZO initiated with BB, was dissolved in 30 ml dry ACN. To the stirred solution were added 0.002 g tetrabutylammonium iodide and 0.15 g pyrrolyl potassium (1.4 mmol) in 2 ml toluene. The system was maintained

6 h at 40°C, then it was filtered and precipitated in diethyl ether. After vacuum drying the yield was of 96%.

The product was characterized by spectral methods.

IR(KBr): 1650 cm^{-1} (N–C=O), 1550 cm^{-1} (Py and PMeOZO) and 700 cm^{-1} (phenyl and Py)

^{1}H-NMR (CDCl$_3$): δ 2.1 (s, CH$_3$C=O), 3.4–4.5 (m, NCH$_2$), 6.8–7.3 (m, C$_6$H$_5$, CH=CH)

^{1}H-NMR (DMSO-d$_6$): δ 2.1 (s, CH$_3$C=O), 3.4–4.5 (m, NCH$_2$), 6.8–7.2 (m, C$_6$H$_5$, CH=CH); 7.7 (s, CH=CH)

2.3. Cyclic voltammetry

Cyclic voltammetry measurements have been carried out in water–PTSA, water–SDS and ACN–TBAFB solvent electrolyte couples at room temperature under nitrogen atmosphere.

2.4. Potentiostatic polymerization of PMeOZO

2.4.1. Self polymerization of PMeOZO
For the self polymerization of PMeOZO, electrolysis cell was prepared by dissolving 1 g/l of PMeOZO, 0.05 M PTSA and/or SDS in distilled water. Constant potential electrolyses were carried out at +0.75 and +1.1 V for 2 h. Electrolyses were also performed in ACN–TBAFB, solvent–electrolyte couple by using 1 g/l PMeOZO and 0.05 M TBAFB at 0.75, 1.1 and 1.4 V for 2 h.

2.5. Polymerization of POX with pyrrole

Electrolyses were performed in the presence of pyrrole at +1.1 V in water–PTSA and/or water–SDS systems. Separate electrolyses were also carried out by dissolving 1 g/l PMeOZO, 1.34 g/l Py and 0.05 M TBAFB in ACN at 0.75, 1.1 and 1.4 V for 1 h.

2.6. Chemical polymerization of PMeOZO

Chemical Polymerization of PMeOZO was carried out in the presence of 1% solution of PMeOZO and 5% solution of FeCl$_3$ in ACN. The same polymerization was performed by adding pyrrole to the same system. After washing with ACN several times, the product was dried in vacuum oven and characterized by FTIR.

2.7. Galvanostatic polymerization of PMeOZO

Constant current electrolysis of PMeOZO was performed with 1.2 g/l of PMeOZO and 0.05 M PTSA in water supplying 200 mA for 7 h.

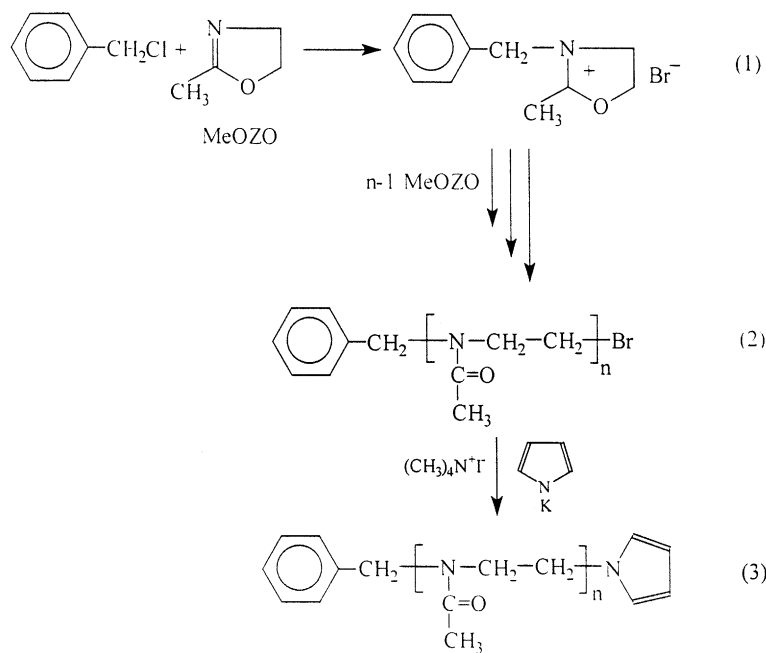## 3. Results and discussion

3.1. Synthesis

Pyrrole end capped (PMeOZO) was prepared by the polymerization of MeOZO initiated by BB, in chloroform ([MOZO] = 3 M, [MOZO]$_0$/[BB] = 25°C, 54°C, in Ar) and subsequent treatment of the bromine terminated polymer with N-pyrrolyl potassium, according to the following reactions. Convenable developed approaches for the N-alkylation of pyrrolle suppose the use of phase transfer catalysts. Quaternary ammonium salts, crown ethers, cryptands were successfully employed [17,18]. Considering these data a small amount of tetrabutylammonium iodide was added to the reaction system, in order to obtain the macromer in relative mild conditions (40°C, 6 h).

3.2. Cyclic voltammetry

Cyclic voltammogram of POX in ACN showed two irreversible oxidation peaks at +0.75 and +1.1 V (Fig. 1a). A decrease in peak intensities was observed with continuous scan revealing a loss of electroactivity. After adding pyrrole to the solution, two peaks at +1.1 and +1.4 V appear in the first run, whereafter the second peak decrease for about 10 runs and further increase thereon. This may be due to the reaction between pyrrole and the pyrrole moiety of the polymer, only, it grows to a certain extent, namely yielding oligomers of certain sizes which then go into the solution without having a chance for further propagation and coat the working electrode (Fig. 1b). Fig. 1c is the cyclic voltammogram of the plain polymer in water. Again the first peak appears at around +0.65 V. The second one (+1.1 V Fig. 1a) is blanketed with oxygen evolution during scans above +1.0 V.

3.3. Potentiostatic polymerization of PMeOZO

3.3.1. Self-polymerization of PMeOZO

For the self-polymerization of PMeOZO carried out in water at 0.75 and 1.1 V, no film formation was observed. Same electrolyses in ACN at 0.75, 1.1 and 1.4 V also resulted in no film formation. Contrary to the self-polymerization of alkyl pyrroles, PMeOZO does not form polymers, most probably due to the rather long chain substitution on the ring nitrogen [19–21].
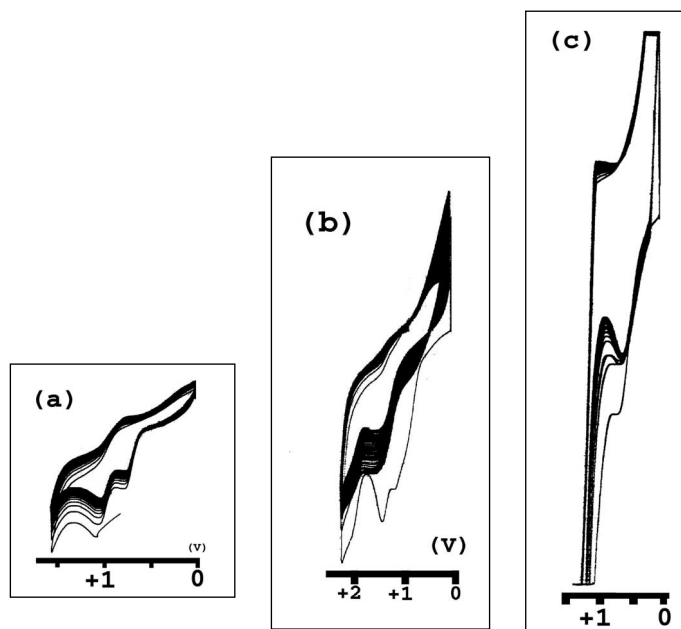
Fig. 1. Cyclic voltammogram of (a) PMeOZO in ACN–TBAFB system, (b) POMEOZO/Py in ACN–TBAFB system and (c) PMeOZO in water–PTSA system.

3.3.2. Polymerization of POX with pyrrole

For the synthesis of graft copolymers of PMeOZO, electrolyses in the presence of pyrrole were performed in both water and ACN systems. For both cases free-standing films obtained from the working electrode were characterized by FTIR spectroscopy. FTIR analysis revealed that those films were the same as the pure polypyrrole film.

Electrolysis with precoated Pt electrodes (with POX) were not possible in both water–SDS (water–PTSA) and ACN–TBAFB systems since POX was soluble in both solvents.

3.4. Chemical polymerization of POX

In the chemical polymerization of PMeOZO, no product was formed. However, in the presence of pyrrole a black powder was obtained. The product was characterized by FTIR spectroscopy. Again the FTIR spectra of the product was the same as the pure polypyrrole.

3.5. Galvanostatic polymerization of PMeOZO

In the galvanostatic polymerization of PMeOZO, no product was obtained.

4. Conclusions

Synthesis of pyrrole-terminated PMeOZO has been successfully achieved. Although the obtained polymer showed good electroactivity, attempts to polymerize it with pyrrole in both chemical and electrochemical conditions failed to produce any graft polymer. This behaviour may be attributed to the limited mobility of the polymeric chains in solution electropolymerization. Moreover, the solubility of the precursor polymer in water and organic solvents prevented the application of surface coating method. Further studies to modify solubility properties of the polyoxazolines and to prepare pyrrole-functional polymers from hydrophobic (2-substituted-2-oxazoline)s and their utilization in electrograft copolymerization with pyrrole are now in progress.

References

[1] Aoi K, Okada M. Prog Polym Sci 1996;21:151.
[2] Kobayashi S, Uyama H. Trends Macromol Res 1994; 1:121.
[3] Shimano Y, Sato K, Kobayashi S. J Polym Sci: Part A; Polym Chem 1995;33:2715.
[4] Kobayashi S, Kaku M, Sawada S, Saegusa T. Polym Bull 1985;13:447.
[5] Schulz RC, Schwarzenbach E. Makromol Chem Macromol Symp 1988;13/14:495.

[6] Cristova D, Velichkova R, Goethals AJ. Macromol Rapid Commun 1997;18:1067.

[7] Mishra MK (Ed.). Macromolecular design: concept and practice. Polym Frontiers Int. (Part 1), New York, 1994.

[8] Kalaycioglu E, Toppare L, Yagci Y, Harbagiu V, Pintela M, Ardelen R, Simionescu BC. Synth Metals 1998; 97:7.

[9] Kizilkaya N, Toppare L, Onen A, Yagci Y. Polym Bull 1998;40:639.

[10] Kızılyar N, Toppare L, Onen A, Yagci Y. J Appl Polym Sci 1999;71:713.

[11] Kizilyar M, Akbulut U, Toppare L, Ozden MY, Yagci Y. Synth Met 1999;104:45.

[12] Alkan S, Toppare L, Hepuzer Y, Yagci Y. J Polym Sci Polym Chem Ed 1999;37:4218.

[13] Alkan S, Toppare L, Yagci Y, Hepuzer Y. J Biomater Sci Polym Ed 1999;10:1223.

[14] Kalacıoğlu E, Toppare L, Yagci Y. Synth Met 2000;108:1.

[15] Öztemiz S, Toppare L, Önen A, Yagci Y. J Macromol Sci – Chem A 2000;37:277.

[16] Yagci Y, Toppare L. Macromol Symp 2000;157:29.

[17] Wang N-C, Teo K-E, Anderson HJ. Can J Chem 1977; 55:4112.

[18] Hallensleben ML, Stanke D, Toppare L. Macromol Chem Phys 1995;196:75.

[19] Ruggerie G, Constantini N, Cagasluti R, Nucci L. Pergola F. Synth Met 1998;92:139.

[20] Tsuchiya M, Matsui S, Sono K, Kojima T. J Appl Polym Sci 1998;70:471.

[21] Diaz AF, Castillo J, Fajardo O, Kanazawa KK, Logan JA, Salmon M. J Electroanal Chem 1982;133:233.