

## **UV-Visible Absorption of Alkyl-Substituted Poly(thiophene) Solutions upon Exposure to Oxygen Gas**

**Rusli Daik\* and S. Maniam**

School of Chemical Sciences and Food Technology, Faculty of Science and Technology,  
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia  
*corresponding author : rusli@pkrisc.cc.ukm.my*

**Abstract :** Poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) were synthesised via oxidative polymerisation in the presence of anhydrous ferric chloride as catalyst. P3HT and P3OT with number average molecular weights of 6,600 and 20,700 g/mol respectively were successfully obtained. The potential of P3HT and P3OT solution as a sensing agent for the detection of oxygen gas was studied. Chloroform, tetrahydrofuran and toluene were used as solvents. The UV-Visible absorption spectra of P3HT and P3OT solutions were recorded before and after the solutions were purged with oxygen gas to study the sensitivity of the polymer solutions towards the presence of oxygen gas. Results showed that both polymers in solution were responsive to the presence of oxygen and as far as response time is concerned, P3HT in chloroform was found to have the best potential as a sensing agent for the detection of oxygen gas.

Received : 05.10.05; accepted : 07.11.07

### **Introduction**

Since early 1980s, conductive polymers have been studied extensively as an important material for semiconductors. Conjugated polymers in interest include polyaniline, polypyrrole and polythiophene [1,2]. These conducting polymers have increased the possibility of designing equipment with a unique combination of optical, electrical and mechanical properties [3,4]. Literatures on conducting polymers show that these materials will have great importance in future and has become an important material in optical studies [5].

However the difficulties in processability that originated from poor solubility have restricted the commercial applications of unsubstituted polythiophenes [6]. Alkyl substituted polythiophenes on the other hand are soluble in most organic solvents. Alkyl substituents strongly influence the properties of polythiophenes. It has been reported that poly(3-alkylthiophene)s also show good environmental stability and electroactivity.

Poly(3-alkylthiophene)s have stirred much interest in the development of future electronic and opto-electronic devices such as LEDs, photovoltaic and photoconductive devices, field-effect transistors and optical modulator devices [7]. Polythiophenes have also been exploited in electrocatalyst [8] and biosensor applications [9]. The study of polythiophene derivatives in the development of optical fibre sensors for the measurement of dissolved and atmospheric gases has also been conducted. Recently, new sensor devices based on polythiophene were developed for space applications, and even incorporated into

hybrid sensor systems [10]. In the past, a variety of oxygen gas sensors on fluorescence quenching [11,12] has been reported. These include the use of ruthenium complexes [13] and aluminum phthalocyanine-polystyrene [14] for oxygen sensing. By incorporating conjugated polymer into sensor devices, an advantage of combining the desired properties of such polymers, for example thermal stability, mechanical strength and processability, with their electronic properties can be achieved [15]. We wish to report here a study on the potential of P3HT and P3OT solutions as sensing agents for the detection of oxygen gas based on UV-Visible absorption.

### **Experimental**

#### **Polymer synthesis**

P3HT and P3OT were prepared by the chemical method described elsewhere [16] with some modification. 3-Hexylthiophene and 3-octylthiophene monomers were polymerised with anhydrous FeCl<sub>3</sub> catalyst in chloroform solution under nitrogen atmosphere. Anhydrous FeCl<sub>3</sub> (8.100g) was added into chloroform in a three neck round bottom flask (250 mL). To the mixture, monomer (2.100g) was added with continuous stirring at 30°C. After 2 hours, the solution was poured into methanol (250 mL). The precipitate was recovered by filtration. The polymer was washed with excess amount of methanol (three times) and stirred (15 minutes) for each time and filtered. The recovered polymer was dried in vacuum oven at 60°C.

### Polymer Characterisation

FTIR and NMR spectra were recorded on a PERKIN-ELMER Model 11310 spectrometer and a FTNMR JEOL EX-400, respectively. GPC (TOSOH HLC 8020) analysis was carried out in THF solution. TGA and DSC thermal analysis were carried out with a Mettler Toledo Star System equipment. UV-Vis spectra were measured with a Varian Model Cary.

### Sensing Test

Three solvents were chosen for sample preparation, which were chloroform, THF and toluene. P3HT (0.004g) was dissolved in respective solvents (4 mL). The solution was diluted to a concentration of  $1.2 \times 10^{-3}$  M before it was analysed using UV-Vis absorption spectrophotometer in the range of 300-500 nm at room temperature. P3HT solution (10mL) was purged with oxygen gas at a constant flow rate. UV-Vis absorption readings were recorded for every 10 minutes until a constant reading was reached. The same procedure was followed for P3OT.

## Results and Discussion

### Polymer Characterization

P3HT and P3OT were obtained as soft and spongy granules with mass recovery of 67% and 70% respectively. Both polymers gave very similar FTIR spectra, with all the characteristic bands expected for alkyl substituted polythiophene and agree with values reported earlier [17].

The  $^1\text{H}$  NMR spectra of both polymers provided sensitive probes for the substitution pattern in the polymer backbone [18]. The protons in the 4-position of the thiophene ring have 4 different chemical environment in a mixture of 4 regioisomers. The  $^1\text{H}$  NMR data proved that P3OT contains an equal distribution of different regioisomers in the polymer chain (1:1:1:1 HT-HT/TT-HT/HT-HH/TT-HT) whereas P3HT failed to provide obvious peaks that corresponded to the presence of regioisomers. Nevertheless, a small peak at 7.00 ppm (TT-HT) was present.

UV-Vis absorption spectra of P3HT and P3OT showed a  $\lambda_{\text{max}}$  at 438.0 nm and 436.0 nm respectively. The maximum absorption in these materials showed the extent of the conjugation which directly affects the observed energy of the  $\pi \rightarrow \pi^*$  transition [19]. P3HT and P3OT in chloroform were very similar in colour; both were bright orange-red.

GPC chromatogram of P3HT showed  $M_n$  and  $M_w$  of  $6.59 \times 10^3$  and  $2.91 \times 10^4$  respectively with a

polydispersity index of 4.41. The  $M_n$  corresponded to 40 repeat units per chain. P3OT has  $M_n$  and  $M_w$  of  $6.65 \times 10^4$  and  $2.07 \times 10^4$  respectively which corresponded to polydispersity index of 3.21 and 107 repeat units per chain (the degree of polymerization were estimated versus polystyrene standards).

The polymers obtained are thermally stable up to 370°C for P3HT and 410°C for P3OT as indicated by TGA thermogram. Both polymers exhibited an obvious difference in their glass transition temperature,  $T_g$ . P3HT gave a  $T_g$  of 80.08°C whereas  $T_g$  for P3OT was 161.60°C. Higher molecular weight for P3OT probably attributes to the less flexible polymer chains as compared to P3HT thus results in higher  $T_g$  for P3OT.

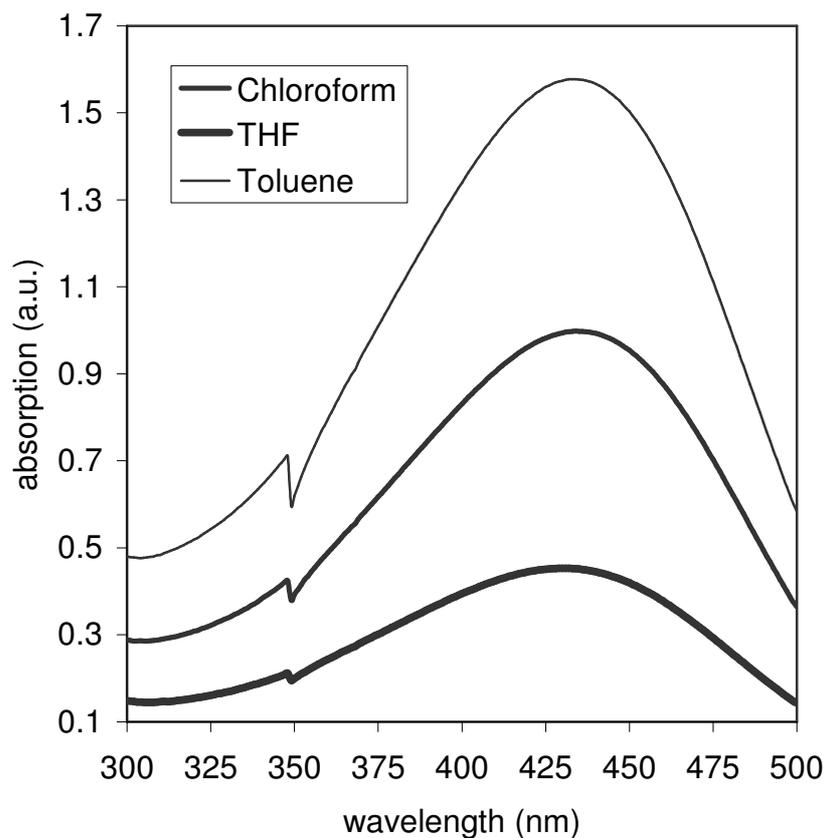
### Sensing test

UV-Vis absorption spectra for the polymer solutions were recorded before and after the polymer solutions were purged with oxygen gas. Oxygen gas was expected to decrease the absorption intensity due to its ability of quenching the chromophore present within the polymers. Quenching may occur by several mechanisms such as coalitional or dynamic quenching, static quenching, quenching by energy transfer and charge transfer reactions [20].

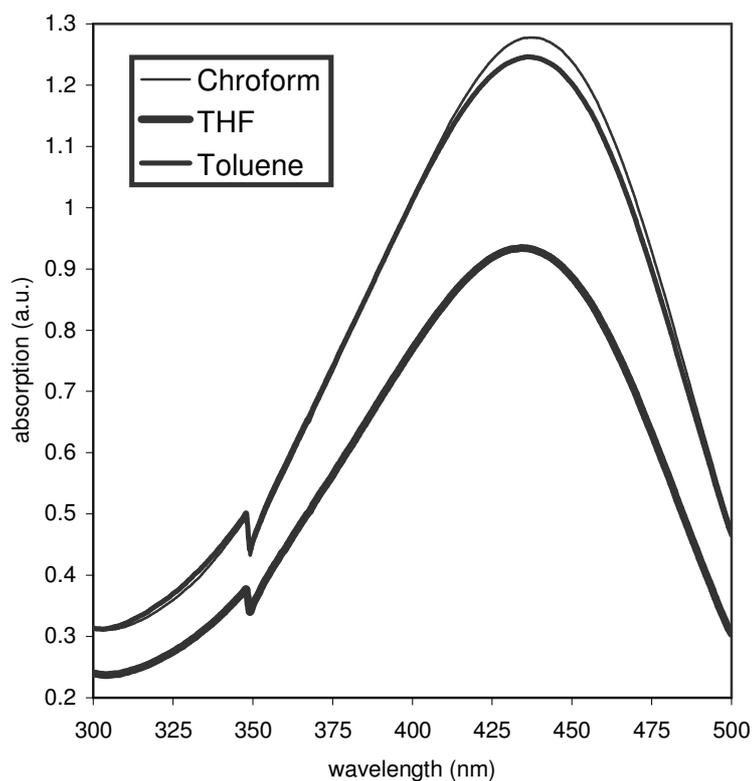
Three non-polar solvents, chloroform, THF and toluene were used to dissolve P3HT and P3OT. Based on the polarizability [21] of oxygen molecules, it dissolves the most in THF, moderately in chloroform and the least in toluene [22].

### P3HT and P3OT solution in toluene

Both P3HT and P3OT in the absence of oxygen gas gave a maximum absorption,  $\lambda_{\text{max}}$  of 434.0 nm. Every 10 minutes after the polymer solution was purged with oxygen gas, the recorded reading of UV-Vis absorption showed a decrease in intensity as shown in Figure 1 and 2, indicating that the polymer solution is responsive optically towards the presence of oxygen gas. Toluene is a good solvent for both P3HT and P3OT but poor for oxygen gas. Thus, it is assumed that the interaction between the polymer chains and oxygen molecules is minimum. The most significant decrease in UV-Vis absorption was at 40<sup>th</sup> minute for both P3HT and P3OT solutions with 0.76% and 0.73% decrease respectively as shown in Figure 3. Generally, both polymer solutions did not show a substantial change in UV-Vis absorption in the presence of oxygen gas



**Figure 1 :** UV-Vis absorption spectra of P3HT in toluene, chloroform and THF



**Figure 2 :** UV-Vis absorption spectra of P3OT in toluene, chloroform and THF

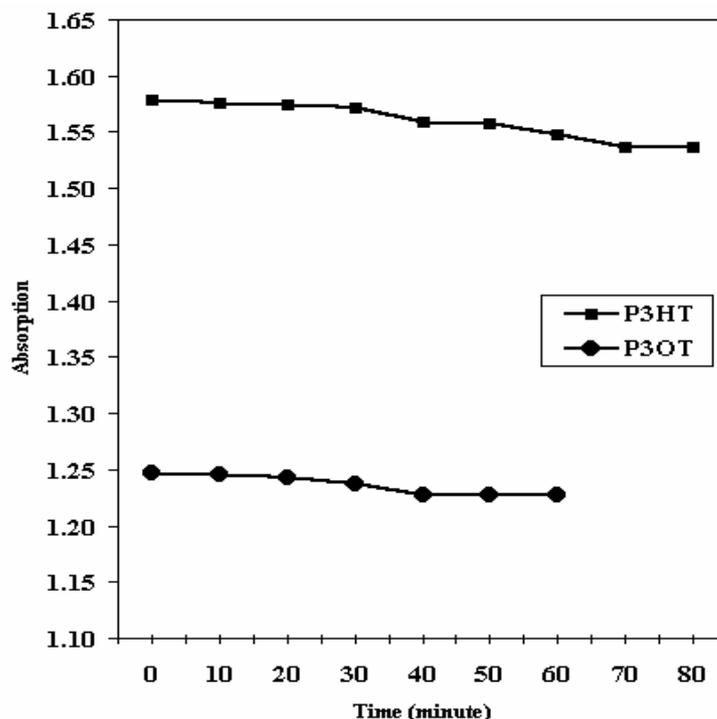


Figure 3 : UV-Vis absorption at  $\lambda_{\max}$  for P3HT and P3OT in toluene

#### P3HT and P3OT solution in THF

In the absence of oxygen gas P3HT and P3OT showed a maximum absorption,  $\lambda_{\max}$  at 430.0 and 434.0 nm respectively. A slow decrease in the UV-Vis absorption was also recorded every 10 minutes; however results were better compared to polymer solutions in toluene. As mentioned earlier, oxygen gas dissolves the best in THF but P3HT and P3OT dissolves the least. An obvious decrease in

absorption for P3HT and P3OT was at the 30<sup>th</sup> and 20<sup>th</sup> minute respectively as shown in Figure 4. P3OT has more repeat units compared to P3HT, giving it a more polar characteristics in spite of the low ability to dissolve. Thus, interaction of P3OT chains with oxygen molecules is predicted to be relatively better as compared to solutions in toluene.

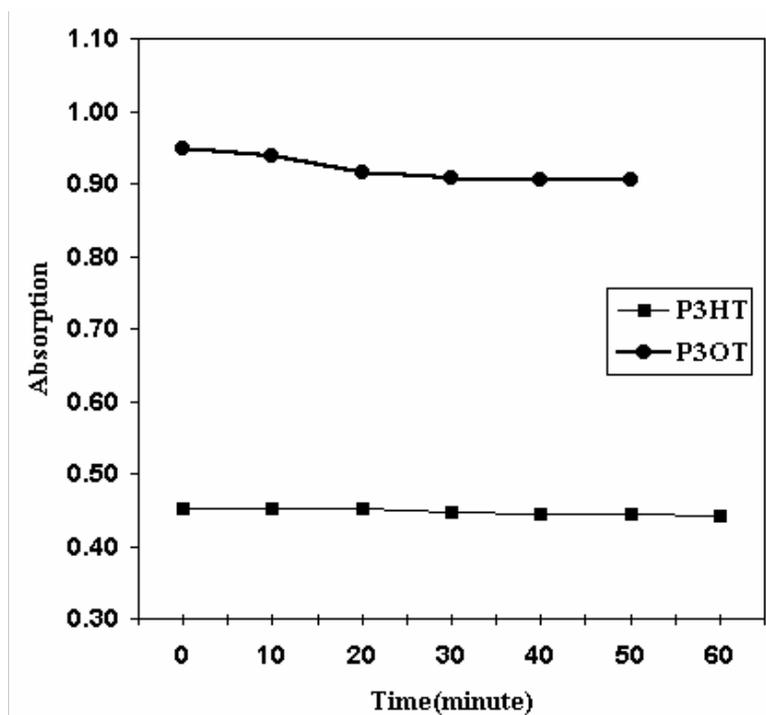


Figure 4 : UV-Vis absorption at  $\lambda_{\max}$  for P3HT and P3OT in THF

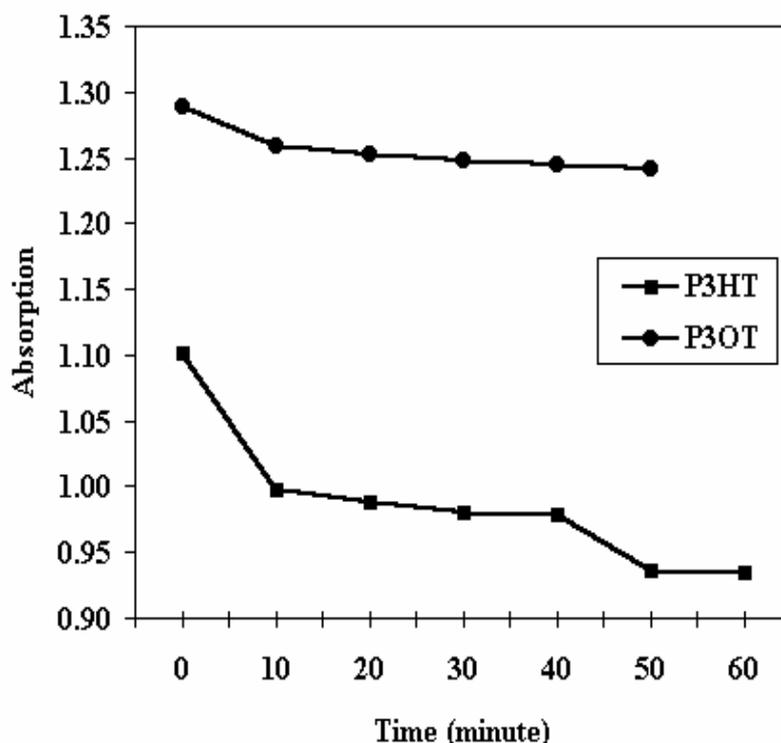


Figure 5 : UV-Vis absorption at  $\lambda_{\max}$  for P3HT and P3OT in chloroform

#### P3HT and P3OT solution in chloroform

Both solutions of P3HT and P3OT in the absence of oxygen gas showed a maximum absorption,  $\lambda_{\max}$  at 434.0 nm. Both polymers showed a significant decrease in absorption as early as 10 minutes after purging the polymer solutions with oxygen gas as seen in Figure 5. P3HT and P3OT showed a decrease of 9.36% and 2.40% respectively. Chloroform is a good solvent for both P3HT and P3OT and a moderate for oxygen gas. Thus, there might be enough polymer and oxygen gas present in chloroform to produce a relatively good response. As far as response time is concerned, P3HT solution was better than P3OT and within all the solvents tested, chloroform was the most appropriate solvent for the preparation of poly(3-alkylthiophene)solution as sensing agent for the detection of oxygen gas.

#### Conclusions

P3HT and P3OT were successfully synthesised with relatively high molecular weight and total mass recovery. Both polymers responded differently depending on the ability of the polymer and oxygen to dissolve in the tested solvents. It has been shown that P3HT and P3OT solution are potentially useful as sensing agents for the detection of oxygen gas. Solution of P3HT in chloroform was found to give the best response towards the presence of oxygen gas.

#### Acknowledgement

Authors are grateful to Professor Dr. Musa Ahmad of Faculty of Science and Technology, UKM for his kind permission to use the facilities in his laboratory.

#### References

- Gustafsson, G., Inganas, O., Osterholm, H., Laakso, J. (1991) X-ray Diffraction and Infra-Red Spectroscopy Studies of Oriented Poly(3-alkylthiophene)s, *Polymer*, **32**, 1574-1580.
- Bredas, J., Chare, R. (1990) Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics. *Kluwer Academic Pub*.
- Cao, Y., Smith, P., Heeger, A.J. (1992) Counter-Ion Induced Processability of Conducting Polyanniline and of Conducting Polyblends of Polyanniline in Bulk Polymers, *Synthetic Metals*, **48**, 91-97.
- Feast, W.J., Tsibouklis, J., Pouwer, K.L., Groenendaal, L., Meijer, C.W. (1996) Synthesis, Processing and Material Properties of Conjugated Polymers, *Polymer*, **37**, 5017-5047.
- Mehamod, F., Daik, R., Ahmad, M. (2003) The Potential Application Of Poly(1,4-Phenylene Diphenylvinylene), *p*-PDV For Oxygen Detection Based On Fluorescence Quenching, *Sensor and Actuators B*, **96**, 537-540.

6. Saxena, V., Prakash, R. (2000) Effect of Steric Hindrance on Junction Properties of Poly(3-alkylthiophene)s Based Schottky Diodes, *Polymer Bulletin*, **45**, 267-274.
7. Grote, J., Taylor, E., Zetts, J., Winter, J., Sanchez, A., Craig, D., Hopkins, F. (2000) Optical Transmission and Thermal Heating Effects Due to Irradiation of Non-Linear Optic and Conductive Polymers Space Based Electrooptic Application, *SPIE Proc. On Photonics for Space Environments Conference VII Vol. 4134* San Diego, CA.
8. Taylor, E., Grote, J., Zetts, J., Winter, J., Sanchez, A., Craig, D. (2000) In Situ High Energy Proton Irradiation of Non-Linear Organic Modulator Materials for Space Environments, *SPIE Proc. On Photonics for Space Environments Conference VII Vol. 4134*, San Diego, CA.
9. Ocon, P., Herrasti, P., Rojas, S. (2001) Galvanostic and Pulse Potential Synthesis of Poly(3-methylthiophene): Polymer As Catalytic Support, *Polymer*, **42**, 2439-2448.
10. Nalwa, H. S. (1997) *Handbook of organic conductive molecules and polymers: Vol. 3. Conductive polymer: Spectroscopy and physical properties*. New York: John Wiley & Sons Ltd.
11. Wolfbeis, O., Weis, L. J. (1988) Fibre Optic Fluorosensor for Oxygen and Carbon Dioxide, *Analytical Chemistry*, **20**, 2028-2030.
12. Mehamod, F.S., Daik, R., Musa, A. (2003) The Potential Application of Poly(1,4-phenylene diphenylvinylene), *p*-PDV for Oxygen Detection Based on Fluorescence Quenching, *Sensors and Actuators B*, **96**, 537-540.
13. Klimant, I., Wolfbeis, O.S., (1995) Oxygen-Sensitive Materials Based on Silicone-Soluble Ruthenium Complexes, *Analytical Chemistry*, **67**, 3160-3166.
14. Amoa, A., Asai, K., Okura, I. (2000) Fluorescence Quenching Oxygen Sensor Using an Aluminium Phthalocyanine-Plystyrene Film, *Anal. Chim. Acta*, **407**, 41-44.
15. Willard, H., Merritt, L., Dean, J. (1965) *Instrumental Methods of Analysis*. Van Nostrand Reinhold, New York.
16. Niemi, V., Knuutila, P., Osterrholm, J. (1992) Polymerisation of 3-alkylthiophenes with FeCl<sub>3</sub>, *Polymer*, **33**, 1559-1562.
17. Chen, T., Wu, X., Rieke, D. (1995) Regiocontrolled Synthesis of Poly(alkylthiophene)s Mediated by Rieke Zinc: Their Characterisation and Solid State Properties, *J. Am. Chem. Soc.*, **117**, 233-244.
18. Barbarella G., Bongini A., Zambianchi, M. (1994) Regiochemistry and Conformation of Poly(3-hexylthiophene) via the Synthesis and the Spectroscopic Characterisation of the Model Configurational Triads, *Macromolecules*, **27**, 3039-3045.
19. McCullough, D., Richard, L., Lowe, D., Jayaraman, M., Anderson, L. (1993) Design, Synthesis and Control of Conducting Polymer Architectures: Structurally Homogeneous Poly(3-alkylthiophene)s, *J. Org. Chem.*, **58**, 904-912.
20. Hobart, H.W., Lynne, L.M., John, A.D. (1974) *Instrumental Methods of Analysis*. New York, D. Van Nostrand Company.
21. McMurry, J. (2000) *Organic Chemistry*. Brooks/Cole, Pacific Grove.
22. Battino, R., Rubin, T.R., Tominaga, T. (1983) The Solubility of Oxygen and Ozone in Liquids, *J. Phys. Chem. Ref. Data*, **12** (2), 164-177.

---