

OPTICAL RESPONSE OF POLY (1,4-PHENYLENE-1,2-DI (*p*-PHENOXYPHENYL) VINYLENE) TOWARDS OXYGEN GAS

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ABSTRACT

This research involved the synthesis of poly (1,4-phenylene-1,2-di (*p*-phenoxyphenyl) vinylene), *dpop*-PDV from di (*p*-phenoxybenzoyl) benzene compound as the monomer. The potential of the produced polymer as sensing reagent for O₂ detection based on fluorescence quenching was studied. Di (*p*-phenoxybenzoyl) benzene was synthesised *via* the Friedel-Crafts benzylation with terephthaloydichloride and biphenylether as starting materials and anhydrous AlCl₃ as the catalyst, while the *dpop*-PDV was synthesized via the McMurry coupling reaction. The polymerization was carried out in THF with TiCl₄ and Zn as the catalyst and reducing agent respectively. Characterization on monomer and polymer had been carried out by using FTIR, GCMS, DSC, TGA, GPC and melting point measurement. Response of the polymer towards oxygen gas was described in terms of fluorescence spectra, repeatability, reproducibility and the response curve. Results obtained showed that the fluorescence intensity decreased upon exposure to O₂ gas, indicating that the polymer was responsive to the presence of the O₂ gas and the sample was found regenerable by flushing the polymer solution with N₂ gas.

1. INTRODUCTION

The area of optical oxygen sensor has witnessed much research activity because of the great interest in the sensor applications for environmental, biomedical and industrial monitoring. Main advantages of optical sensors over the traditional electrochemical oxygen electrodes are low oxygen consumption, compatibility with advanced integrated optical technology and the absence of electrode poisoning by the organic compounds or by external electromagnetic field¹. Many optical oxygen sensors consist of organic dyes such as aromatic polycyclic hydrocarbons (pyrene and its derivatives, quinoline and phenanthrene) immobilized in an oxygen permeable polymer matrix^{2,3}. Most optical oxygen sensors in the literature are based on fluorescence quenching of the fluorophore such as transition-metal complex (e.g. ruthenium(II) (Ru(II)) complexes), embedded in polymer or in sol-gel matrices^{4,5,6}. Much progress has been made on transition-

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metal complex-based oxygen sensors. These sensors however are susceptible to several limitations such as short lifetime (ns- μ s range)⁷ and low sensitivity (fluorescence intensity variation less than 10 times between oxygen concentration of 0-100%)⁵. Poly(arylene vinylene)s, PAVs are of special interest in the field of materials for solid state electronic^{8,9,10}. The use of such materials in device configuration has been demonstrated for instance, in light emitting diodes (LEDs)^{11,12}, batteries¹³ and as well as in sensors¹⁴. Most researches on application of PAV as sensing reagent in optical fiber sensor are based on either conductivity or redox behaviour of the material¹⁵. However the exploitation of the unique property of PAV, such as fluorescence is not widely reported.

In this paper, we report our attempt to discover the possibility of using a PAV type polymer, namely poly(1,4-phenylene-1,2-di(*p*-phenoxyphenyl)vinylene), *dpop*-PDV as sensing reagent for oxygen gas detection which is based on the fluorescence properties of the polymer.

2. EXPERIMENTAL

2.1 Monomer synthesis

Terephthaloyldichloride (10.00g, 0.049mol) was added to biphenylether (150mL, in excess) in a three neck round bottom flask (250mL) equipped with a magnetic stirring bar, a condenser and a thermometer under dry nitrogen atmosphere. The mixture was stirred and cooled in an ice-bath. Powdered anhydrous aluminium(III)chloride (15.12g, 0.113mol) was added in small portion over a period of 30 minutes. The reaction mixture was then refluxed for 5 hours, cooled and poured into ice-water (200mL). The organic portion of the mixture was extracted into chloroform (3x50mL) and all the organic extracts were collected in the same container. After evaporating the solvent, a white solid was recovered and re-crystallised from toluene (3x) to give a pure di(*p*-phenoxybenzoyl)benzene. Figure 1 showed the synthesis route of di(*p*-phenoxybenzoyl)benzene.

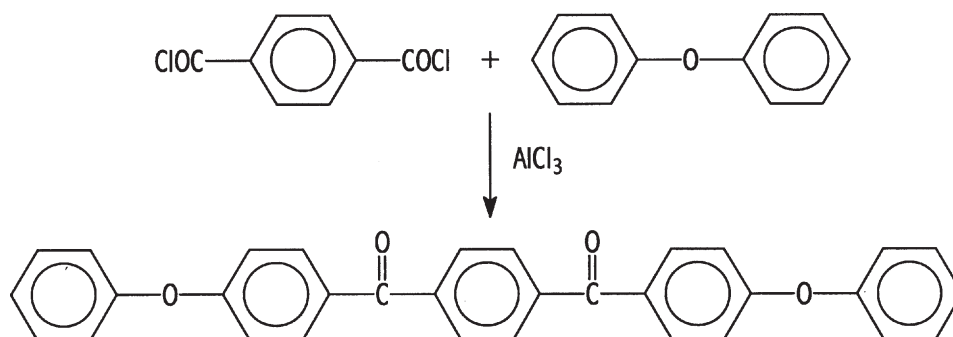


Figure 1 : The synthesis route of di(*p*-phenoxybenzoyl)benzene

2.2 Polymer synthesis

Zinc dust (2.35g, 0.036mol) was added to THF (150mL) in a three neck round bottom flask (250mL) fitted with condenser, a magnetic stirring bar and a thermometer under nitrogen atmosphere. Titanium (IV) chloride (2.27g, 0.012mol) was then added to the mixture at about 0°C while stirring rapidly. The mixture was then refluxed for 3 hours. After adding di(*p*-phenoxybenzoyl)benzene (3.00g, 0.006 mol) at room temperature, the mixture was further refluxed for 20 hours. At about 0°C, dilute HCl (200mL, 2M) was added to the mixture and the product was extracted into chloroform (3x50mL). The extracts were washed with saturated solution of NaCl, dried over anhydrous MgSO₄ and the solvent was evaporated to give a concentrated polymer solution. The polymer was then re-precipitated into methanol to give a bright yellowish powder of *dpop*-PDV. Figure 2 showed the synthesis route of *dpop*-PDV.

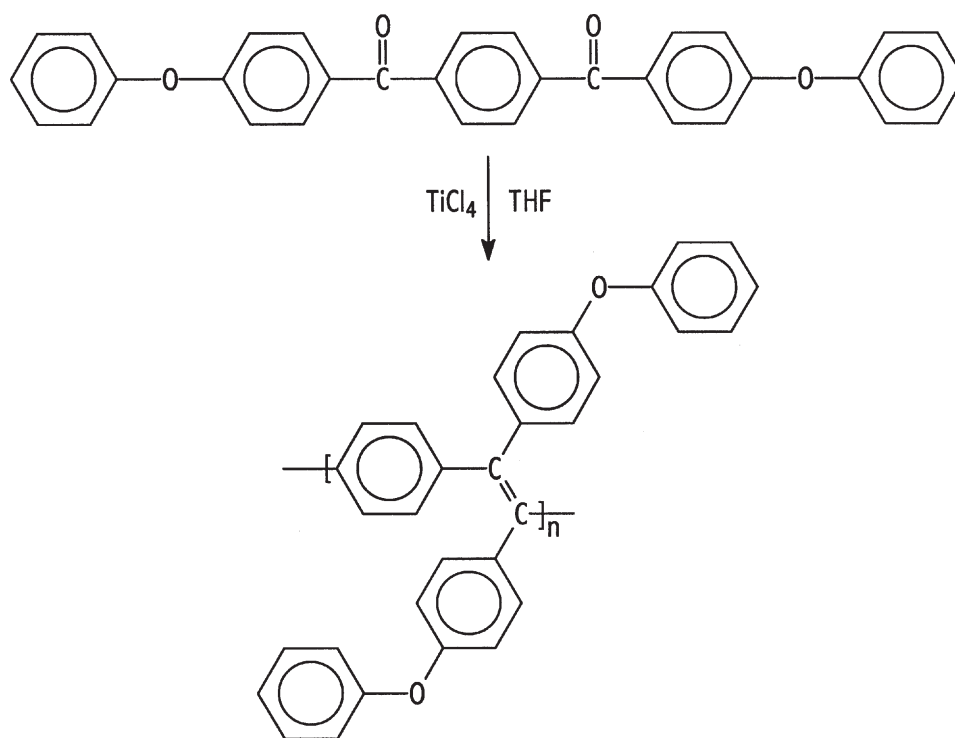


Figure 2 : The synthesis route of *dpop*-PDV

2.3 Preparation of the *dpop*-PDV solution

The *dpop*-PDV (17mg) was dissolved in DMF (50mL) to form homogeneous solution. The solution was used for analytical determinations using Spectrometer Luminescence LS-50B.

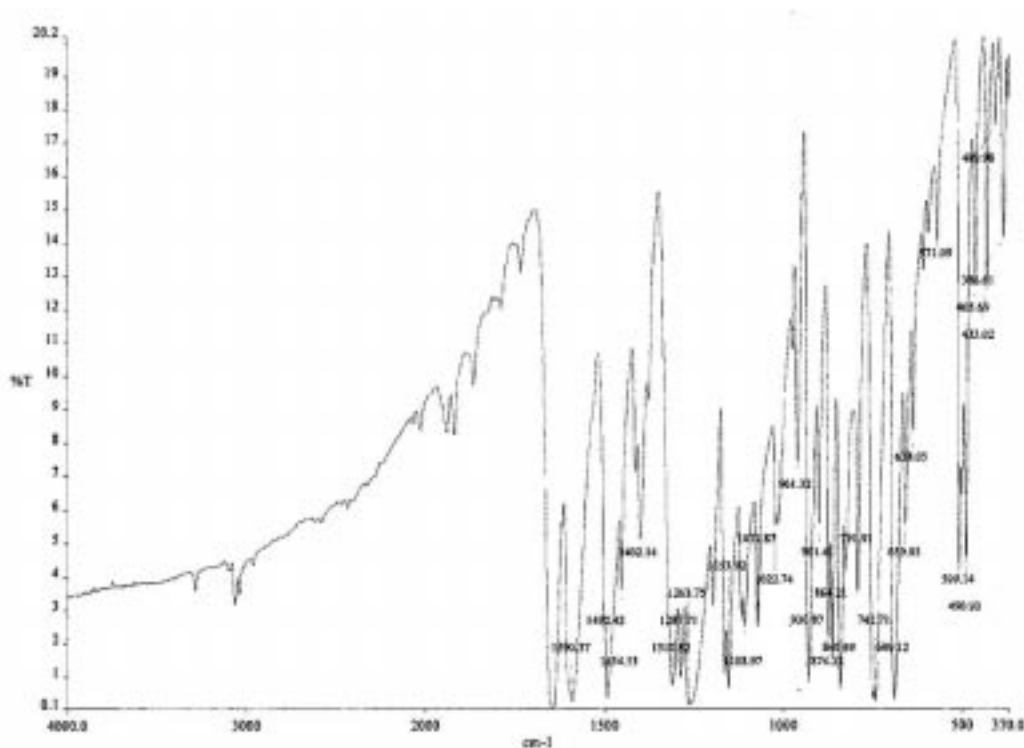


Figure 3 : The FTIR spectrum of di(*p*-phenoxybenzyl)benzene

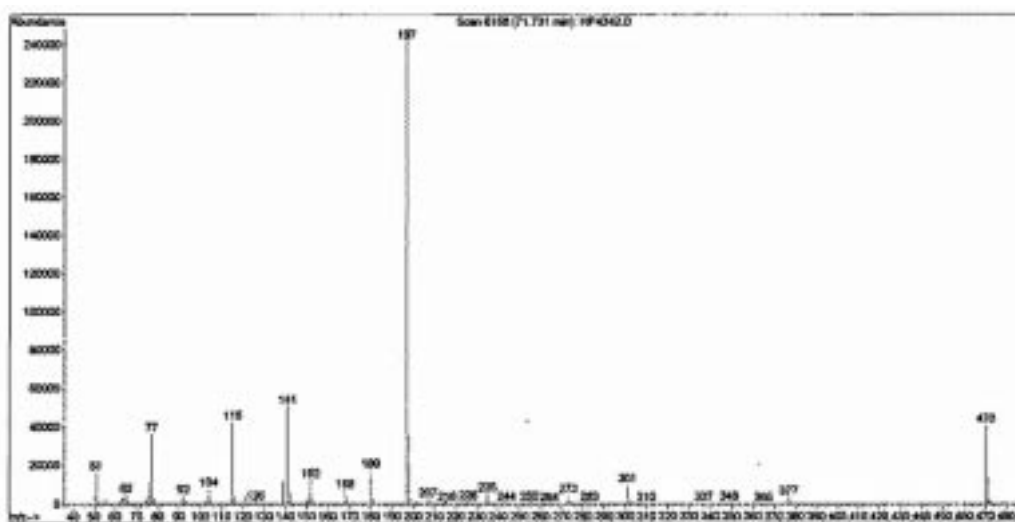


Figure 4 : The MS spectrum of di(*p*-phenoxybenzyl)benzene

3. RESULTS AND DISCUSSION

3.1 Monomer

The structure of monomer di(*p*-phenoxybenzoyl)benzene was confirmed by elemental and spectroscopic analyses. Figure 3 showed the FTIR spectrum of the monomer recorded on KBr pellet. The peak corresponding to conjugated ketone carbonyl stretching can be seen at 1645cm^{-1} . The peak at 1587cm^{-1} can be assigned to the aromatic carbon skeleton vibration mode. The characteristic peak for ether could be seen at about 1300cm^{-1} to 1000cm^{-1} . According to the elemental analysis, the monomer was the desired compound and the mass spectrum in Figure 4 showed the expected molecular ion.

3.2 Polymer

The polymer is soluble in common organic solvent including chloroform, THF and toluene. The UV-Vis absorption spectrum was recorded for *dpop*-PDV in chloroform. The spectrum in Figure 5 obtained for *dpop*-PDV showed peaks at 292nm and 356nm. The peak at 356nm can be attributed to the presence of conjugation sequence along the *dpop*-PDV backbone chain while peak at 292nm can be attributed to the secondary absorption band of delocalized electrons within pendant biphenylether ring.

The glass transition temperature, T_g for *dpop*-PDV was about 195°C as measured by differential scanning calorimetry (DSC). It was shown by thermogravimetric analysis that the polymer is thermally stable up to above 350°C under nitrogen atmosphere. The M_n and M_w of *dpop*-PDV as measured by GPC were 1200 and 1500 respectively and the peaks present on the trailing edge of the chromatogram in Figure 7 correspond to the telomeric units.

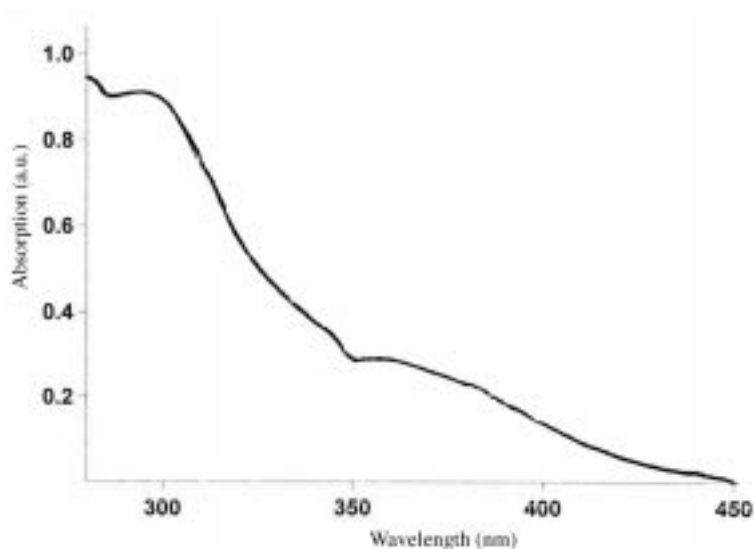


Figure 5 : The UV-Vis spectrum of *dpop*-PDV

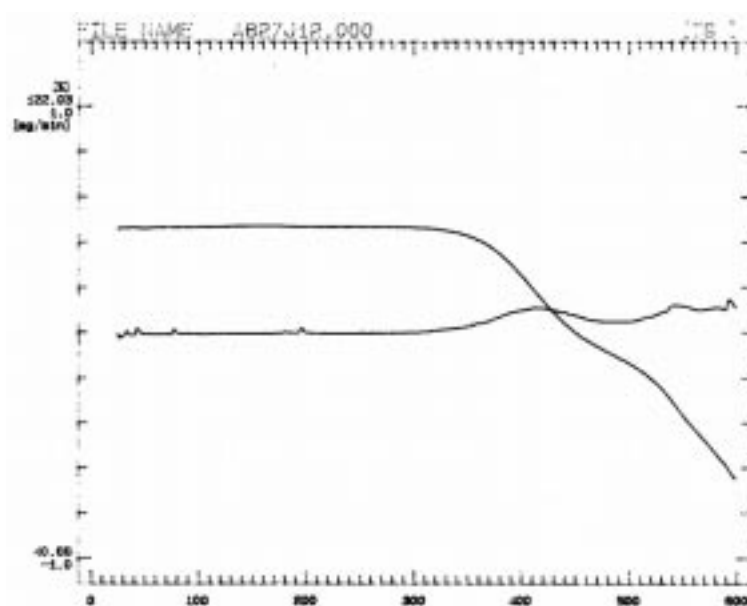


Figure 6 : The TGA thermogram of dpop-PDV

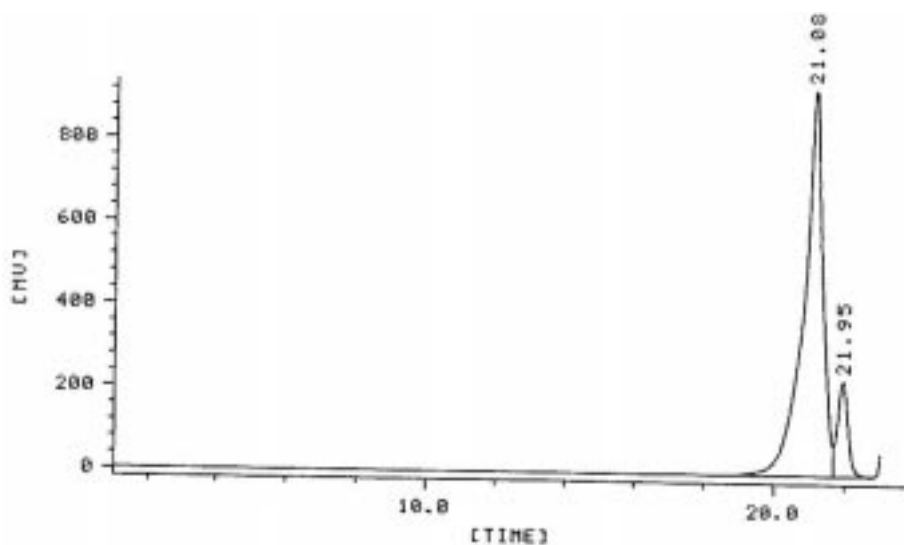


Figure 7 : The GPC trace of dpop-PDV

3.3 Sensing characteristics

The excitation spectrum obtained for dpop-PDV (Figure 8) showed a clear image to the respective fluorescence spectrum where the polymer was excited at 463 nm and the emission was observed at 515 nm. This could be due to the vibrational spacing in the ground state (S_0) that is often similar to the first excited singlet state (S_1)¹⁶.

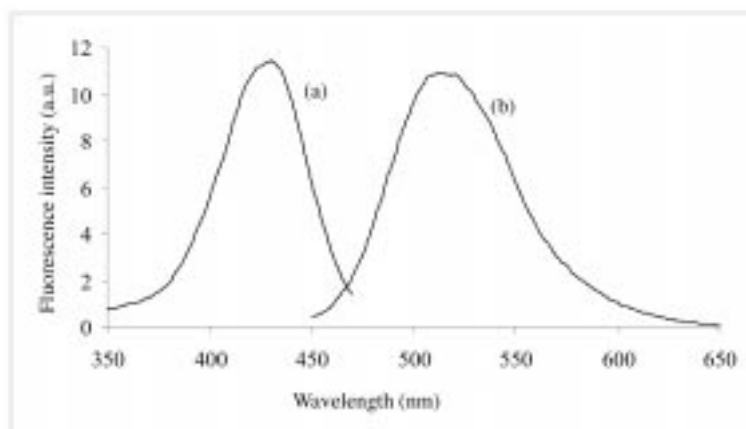


Figure 8 : The excitation (a) and emission (b) spectra of *dpop*-PDV (λ_{ex} : 463nm, λ_{em} : 515nm)

Oxygen is known as a good quencher. Quenching could be generally defined as the destruction of the fluorescence intensity¹⁷. Figure 9 showed the spectrum of *dpop*-PDV solution when exposed to O₂ gas. The spectrum obtained showed that the fluorescence intensity decreased when the polymer was exposed O₂ gas as expected. In photostability study, *dpop*-PDV solution was irradiated with visible light under nitrogen atmosphere. However, the fluorescence spectrum obtained did not show the expected result. Throughout the 9 hours of irradiation, the fluorescence intensity of *dpop*-PDV continuously decreased. This observation showed that the *dpop*-PDV is either very sensitive to the presence of O₂ gas or it is not stable when exposed to the spectrometer light source used in the experiment.

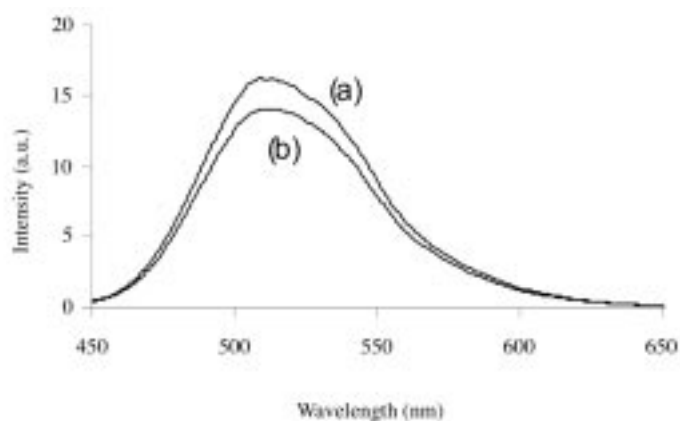


Figure 9 : The fluorescence spectrum of *dpop*-PDV before (a) and after (b) quenching with O₂ gas

Repeatability refers to the response generated by single sensing reagent when used to determine the same amount of O₂ gas for several times. Reproducibility on the other hand, refers to the response generated by different sensing reagent when exposed to the same amount of O₂ gas. The RSD for the repeatability was found to be 2.36% while for reproducibility was 6.03% for four measurements taken. The RSD value for repeatability that was slightly higher than that of the reproducibility was possibly due to errors during sample preparation.

In this study, the sensing reagent was regenerated by flushing the polymer solution with N₂ gas. The response time of the sensor for both on going from nitrogen to oxygen and from oxygen to nitrogen was around 2 minutes. However, the *dpop*-PDV was not responsive towards O₂ gas after 10 minutes of regeneration process. This matter and other aspects will be pursued by characterising the polymer further.

4. CONCLUSION

It has been shown that the *dpop*-PDV solution was responsive to the presence of O₂ gas and was regenerable on flushing with N₂ gas. Regeneration process showed promising result since reversible changes in the emission spectra were observed, although it occurred within only about 10 minutes of the process. Therefore, provided that the method to refine the properties of the polymer is available, detection for O₂ gas could be much better.

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