CHAPTER V

SELECTIVITY IMPROVEMENT OF POLYPYRROLE/POLY(METHYL METHACRYLATE) BLEND TOWARD FLAMMABLE CHEMICALS IN LACQUER

Selectivity Improvement of Polypyrrole/Poly(methyl methacrylate) Blend toward Flammable Chemicals in Lacquer

Abstract

A film of α-naphthalene sulfonate doped polypyrrole/poly(methyl methacrylate), PPy/α-NS$^-$/PMMA, obtained from solution mixing was successfully used as sensing material for acetone vapor in lacquer with a high degree of selectivity based on electrical conductivity over acetic acid. Compared with pure PPy/α-NS$^-$, the selectivity ratio of acetone/acetic acid response of PPy/α-NS$^-$/PMMA blend with a PMMA/PPy weight ratio of 3.0 was ca. 3.8 times higher. The film was found to be insensitive to moisture unless the relative humidity was lower than 20 %RH in which the selectivity ratio of acetone/acetic acid response was enhanced. The time required to reach the equilibrium signal at relative humidity of 20 – 30 %RH was 6 - 15 min; it was as high as 20 - 26 min at 50 - 70 %RH.

Keywords: conductive polypyrrole, poly(methyl methacrylate), flammable chemical sensor, blends, selectivity

1. Introduction

Conductive polypyrrole has been utilizing as sensing material for many gases and vapors [1-4]. The variety of gases and chemical vapors that change the electrical conductivity of PPy reflects its low selectivity. To overcome this problem, many researchers fabricated sensor arrays consisting of conductive polymeric sensing materials, e.g. PPy, polyaniline, polythiophene; and their derivatives [5,6]. Even though those arrays may work well on the basis of pattern recognition, they have to be initially calibrated with all target gases. In addition, they are complicated and need an expensive software to operate. In order to develop an inexpensive, portable, and on-line polymer based conductive sensor for flammable chemicals, i. e. acetone in lacquer, the sensing material requires a high degree of selectivity toward the target molecule, acetone, over interferences, i.e. acetic acid, which is a component in lacquer but not highly flammable, and water, which is present in the moist air. In a previous study of our group, a film of PPy/α-NS$^-$/PMMA blend prepared from solution mixing showed enhanced responses toward liquid acetone and a reduced response toward water [7]. Nevertheless, the response to acetone was almost the same as the response to glacial acetic acid. This paper extends that previous study to the vapor phase, in an attempt to optimize the selectivity for acetone by varying the weight ratio of PMMA in the blend. The optimized PMMA/PPy weight ratio was then used to study the effect of relative humidity on the response toward acetone and acetic acid vapors.

2. Experimental

2.1 Materials

Pyrrole monomer (AR grade, Fluka) was purified by distillation under reduced pressure prior to use. Ammonium persulfate (AR grade, Aldrich) and α-naphthalene sulfonic acid, sodium salt (AR grade, Fluka) were used as the oxidant and as the dopant, respectively, for an *in situ* doped oxidative polymerization. Poly (methyl methacrylate), PMMA (Polysciences, INC.) and toluene (HPLC grade, J.T. Baker) as solvent for solution mixing were used without purification. The chemicals for the electrical response tests were acetone (AR grade, Lab-Scan) and acetic acid glacial (AR grade, Lab-Scan).

2.2 Sample Preparation

The PPy/α-NS$^-$ was chemically synthesized according to the method reported earlier [8]. The dopant to pyrrole monomer molar ratio used was 1/12. With this feeding dopant ratio, as compared to the ratio of 1/5 in the previous work [7], the sensor responses to liquid acetone and glacial acetic acid were similar but the response to liquid water was ca. 3 times lower [9]. This PPy was aged in dry air (40-50 % relative humidity) at atmospheric pressure for 5 months before the experiments. During this period, PPy/α-NS$^-$ became non-aging: its specific conductivity reached a steady state value. 0.05 g of PPy powder was ground and pressed by a hydraulic press at 60 kN into a pellet with a diameter of 2.5 cm and a thickness between 80 – 90 μm, as measured by a thickness gauge (Peacock model PDN 12N). Solution mixing was done by first dissolving PMMA in 12.0 cm^3 toluene using an ultrasonic bath. When the polymer was completely dissolved, 0.6 g of PPy/α-NS$^-$ was added. The ultrasonification was further carried out for only 2 min to avoid chain degradation. The weight ratios of PMMA to PPy/α-NS$^-$ were fixed at 1.0, 2.0, 3.0 and 4.0. The films of these mixtures were cast on a 2.2 cm x 2.2 cm glass slide. After open-air drying for 6 hours, free-standing films of PPy/α-NS$^-$ /PMMA were obtained with thickness values of 100 – 110 μm.

2.3 Surface Compositions, Electrical Properties of PPy/α-NS$^-$ and PPy/α-NS$^-$/PMMA films

The surface compositions of PPy/α-NS$^-$/PMMA samples with different weight ratios of PMMA to PPy/α-NS$^-$ were extracted from the C 1s region of X-ray photoelectron spectra obtained using a Perkin Elmer model PHI 5400 X-ray photoelectron spectrometer. The non-monochromatic Mg Kα radiation with photon energy of 1253.6 eV was selected as X-ray source with a power of 300 W (15 kV x 20 mA). The pass energy and the take-off angle were 17.90 eV and 45^o, respectively. The relative intensity and FWHM of C components in PMMA were fixed at the values reported by Wagner [9]. The specific conductivity, σ, of the PPy/α-NS$^-$ pellet and PPy/α-NS$^-$/PMMA films were measured by a custom-made four-point probe (linear array) conductivity meter [8].

2.4 Electrical Conductivity Response of PPy/α-NS$^-$ and PPy/α-NS$^-$/PMMA films toward Chemical Vapors

The flow system for testing the sensor response consisted of a humidity-control set (the water container and the desiccant), a chemicals container, and an exposure chamber which contained a four-point probe and a thermohygrometer (Cole-Parmer, model P-03313-86). The acetone or acetic acid in the chemicals container was vaporized and flown into a closed loop system for at least 30 min before feeding it to the exposure chamber. The saturated vapor concentration of acetone and acetic acid in N_2 at 25 ^oC were 30.3 and 2.0 vol.%, respectively [10]. To study the effect of relative humidity, dry N_2 was flown in to the system passing through a water container or a desiccant in order to increase or decrease the relative humidity in the exposure chamber: 20, 30, 50, and 70 ± 3 %RH at 25 ± 1 ^oC. The consistent changes in the specific conductivity of the PPy/α-NS$^-$ pellets and the

PPy/α-NS$^-$/PMMA films upon exposures to acetone or acetic acid vapors under the above conditions will be reported as the percentage of the specific conductivity change, $(\sigma - \sigma_i) / \sigma_i \times 100\%$, where σ is the specific conductivity at equilibrium state after exposures and σ_i is the specific conductivity of the fresh sample.

3. Results and Discussion

3.1 Surface Compositions and Electrical Properties

The presence of PPy/α-NS$^-$ at the surfaces of the PPy/α-NS$^-$/PMMA films with various weight ratios of PMMA are shown in Figure 1 in term of PPy fraction at the surface, along with the specific conductivity values of all samples. The PPy fraction at the surface is higher than the blend composition. This indicates the suspending at the surface of PPy particles during film casting and drying. The PPy fraction at the surface was unusually high when the weight ratio of PMMA/PPy was 4.0, reflecting a very high degree of incompatibility when the concentration of PMMA in toluene solution was too high. The specific conductivity values of these films had a good correlation with the weight ratios. With the 1:1 weight ratio of PMMA/PPy, the specific conductivity decreased by 3 orders of magnitudes. Upon further increasing PMMA proportion, small decreases in specific conductivity values were observed. This also corresponds to small decreases in PPy fraction at the surface. The unusual high PPy fraction and the low specific conductivity at the weight ratio of 4.0 suggest that the specific conductivity was a bulk property, not a surface property.

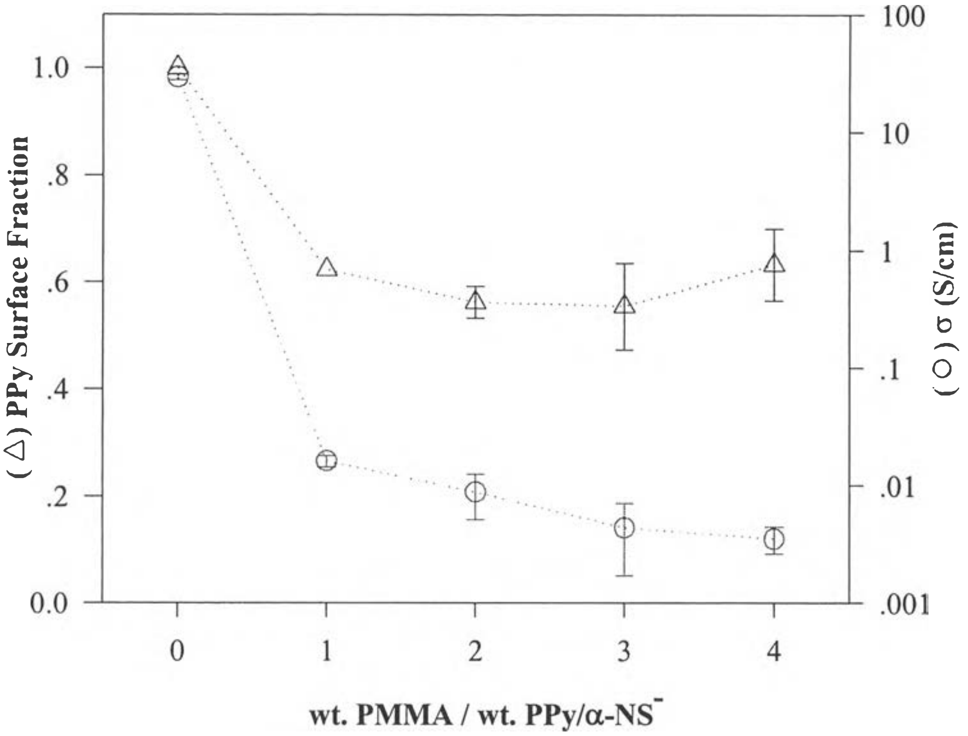

Figure 1 (△) The fraction of PPy at the surfaces of the PPy/α-NS$^-$ pellets and the PPy/α-NS$^-$/PMMA films with various weight ratios of PMMA; and (○) their specific conductivity values, measured in N_2 at 25 ± 1°C and at 50 ± 5 %RH.

3.2 Electrical Conductivity Response toward Chemical Vapors

Figure 2a shows the percentages of changes in electrical conductivity values of samples upon exposures to saturated acetone and acetic acid vapors. With increasing proportion of PMMA, the responses toward both chemicals were enhanced. The acetone response became more dominant at PMMA/PPy weight ratios larger than 1.0. The ratios of acetone/acetic acid response were 2.0 - 2.6 (Figure 2b).

The negative changes in electrical specific conductivity of the samples are believed to be mainly induced by swelling of PMMA in acetone and acetic acid [11]. A swollen PMMA separated conducting PPy apart and reduced the specific conductivity of the material. The response toward acetone was more enhanced than that of acetic acid with increasing PMMA proportions, due to the greater swelling of PMMA in acetone.

3.3 The Recovery Factor after Exposures to Chemical Vapors

When the samples were once exposed to acetone or acetic acid vapors, their specific conductivity values could be recovered after purging with N_2. We define the ratio of the recovered specific conductivity values to the fresh values (σ_{1st}) as 'the recovery factor'. The PPy/α-NS$^-$ pellets and the PPy/α-NS$^-$/PMMA films with various weight ratios of PMMA possessed different recovery factors after the exposures to acetone or acetic acid vapor for 4 – 5 times, as shown in Figure 3.

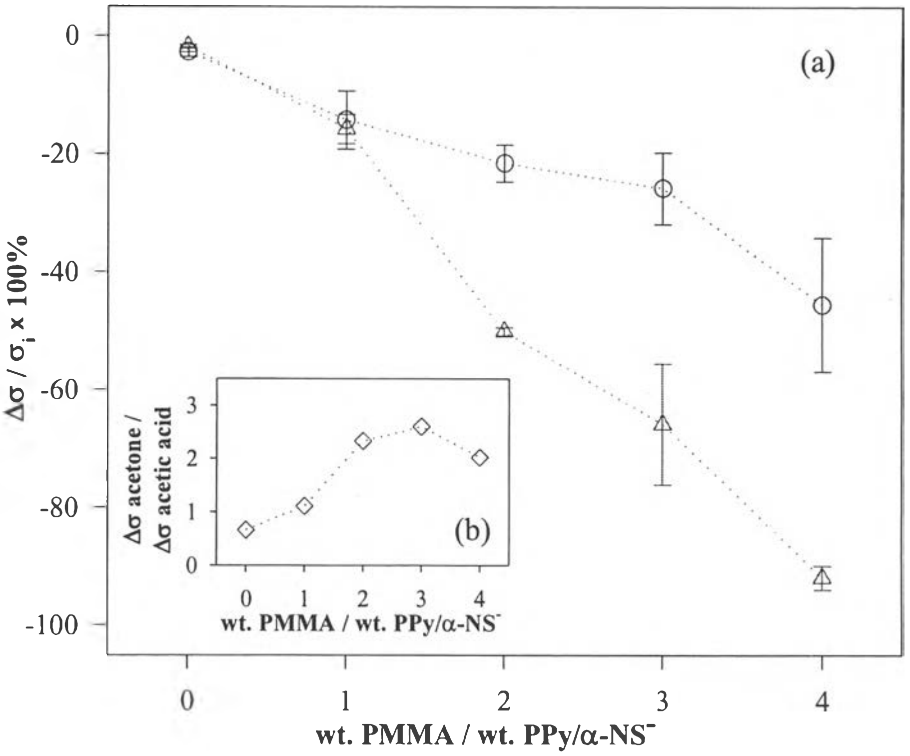

Figure 2 a) The percentages of changes in specific conductivity values of the PPy/α-NS⁻ pellets and the PPy/α-NS⁻/PMMA films with various weight ratios of PMMA during the exposures to: (△) saturated acetone vapor, and (○) saturated acetic acid vapor in N_2: b) their acetone/acetic acid response ratios, measured at 25 ± 1°C and at 50 ± 5 %RH.

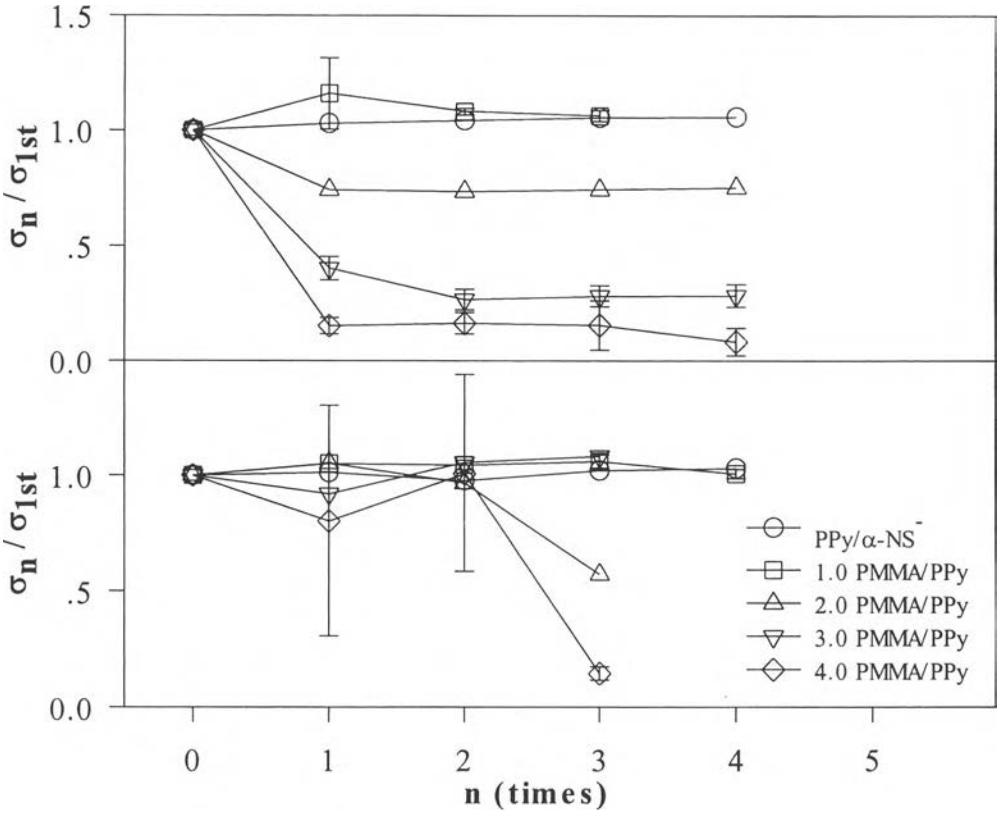

Figure 3 The ratios of recovered specific conductivity values (σ_n) to the fresh values (σ_{1st}, n = 0) of the PPy/α-NS$^-$ pellets and the PPy/α-NS$^-$/PMMA films with various weight ratios of PMMA after the exposure to: a) saturated acetone vapor, and b) saturated acetic acid vapor in N_2, for 3 - 4 times, measured at 25 ± 1°C and at 50 ± 5 %RH.

The PPy/α-NS$^-$ pellets and the 1.0 PMMA/PPy film showed good recoveries after exposures to acetone or acetic acid over 4 repetition times. The other films with weight ratios of 2.0, 3.0, and 4.0 had fair or poor recoveries after exposures to acetone, in fact they showed unpredictable recovery factors after exposures to acetic acid.

In terms of selectivity factor, PMMA/PPy films with weight ratios of 2.0 – 4.0 are acceptable and the film with a weight ratio of 3.0 is the most promising sensing material for our purpose. Nevertheless, due its fair recovery factors, only the fresh films were used in the next experiment.

3.4 Effect of Humidity on Chemical Vapor Response of PPy/α-NS$^-$/PMMA

The electrical responses, of the fresh PMMA/PPy films with a weight ratio of 3.0, toward saturated acetone and acetic acid vapors at different relative humidity values are shown in Figure 4. The acetone response seemed to be insensitive to the humidity variation except at 20 %RH where the response was enhanced up to 80-85%. The acetic acid response was insensitive to the humidity variation in the whole range of study.

The PMMA/PPy film has been previously reported to be insensitive to water, relative to the pure PPy/α-NS$^-$ [7] consistent with the above results. It is conceivable that during purging of the exposure chamber with dry N_2 to achieve a relative humidity of 20 %RH, some of the residual solvents in the film, e.g. water and toluene, might have been removed. When there was less moisture content in the film, the acetone response increased, according to the increase of accessible active sites of hydrogen bonding donor, -NH- [8]. The possible loss of toluene could lead to a higher ordering in the film which was beneficial for acetone detection: there were more ordered structures to be destroyed by acetone [8].

Let's now turn to the time needed for the sensing materials to reach equilibrium signals (t_{eqb}) after chemical vapors were injected into the system (Figure 4). Since t_{eqb} is strongly dependent on the flow system used, we will compare t_{eqb} only from our different experiments. The t_{eqb} values of 3.0 PMMA/PPy films were 8 –12 min at 20 – 30 %RH and increased as high as 20 - 26 min at 50 - 70 %RH. Even though the absolute change in electrical signal was not altered by humidity; the time needed for equilibrium was much affected at very high humidity. At high moisture levels, the high concentration of water, which is an extremely poor solvent for PMMA, may have hindered the swelling effect of PMMA/PPy induced by acetone vapor.

The t_{eqb} values observed from exposures of acetic acid vapor were generally longer, 36 – 45 min, due to a lower evaporation rate and vapor pressure of acetic acid as compared to acetone [12]. The humidity did not affect t_{eqb} for acetic acid exposure. Considering the response of pure PPy to acetic acid vapor and the slope of acetic acid response in Figure 2, the interaction of acetic acid with PPy was more dominant than the interaction with PMMA (swelling). Hence, the presence of water at high humidity did not effect the acetic acid response as in the case of acetone response.

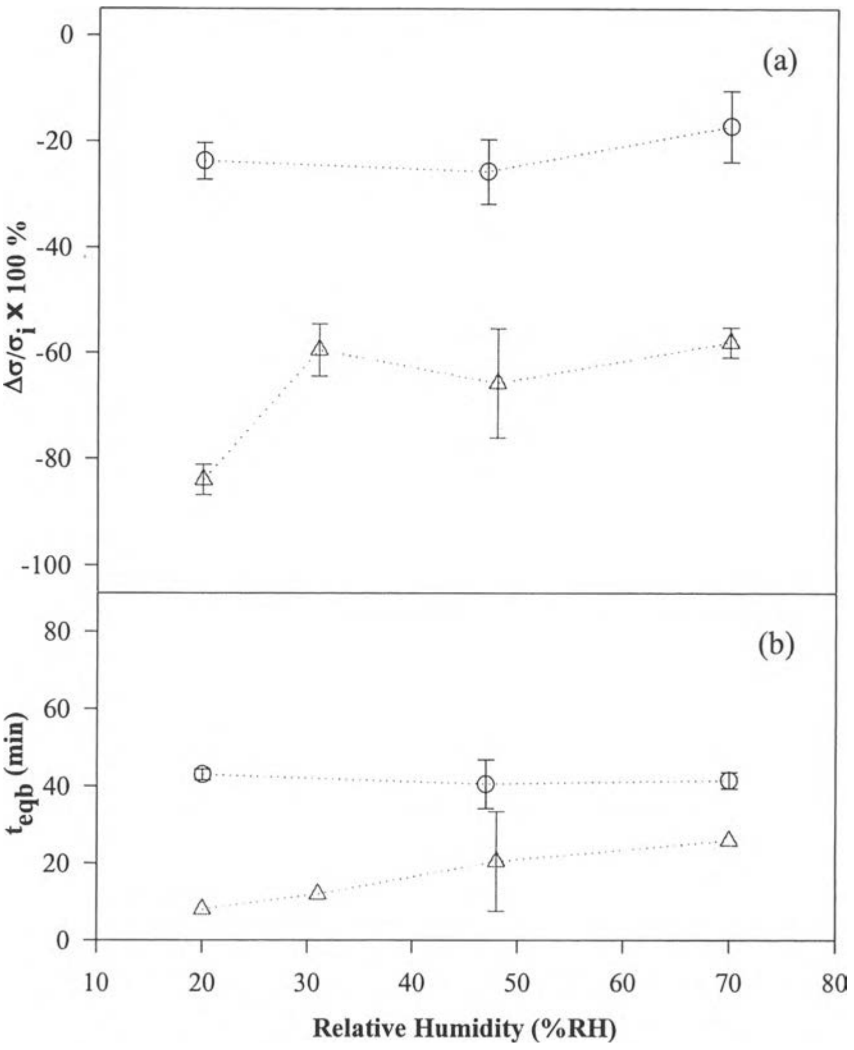

Figure 4 a) The percentages of changes in specific conductivity values of the PPy/α-NS⁻/PMMA films with PMMA/PPy weight ratio of 3.0 during the exposures to: (△)saturated acetone vapor; and (○) saturated acetic acid vapor: b) the time needed to reach the equilibrium conductivity changes when exposed to: (○) saturated acetone vapor; and (△) saturated acetic acid vapor, as a function of relative humidity, measured at 25 ± 1 °C.

4. Conclusion

The film of PPy/α-NS$^-$/PMMA blend cast from solution of toluene was used as the sensing material for acetone vapor in lacquer with a high degree of selectivity over acetic acid and moisture. Compared to the selectivity ratio of acetone/acetic acid response of pure PPy which was 0.7, the selectivity ratio of PPy/α-NS$^-$/PMMA blend with PMMA/PPy weight ratio of 3.0 was about 3.8 times higher. However, this material could be used only once. This selectivity ratio was found to be unaffected by a change in humidity except at very low relative humidity of 20% where the selectivity ratio was enhanced. The possible reason was the loss of water from the film at low relative humidity, increasing the amount of active sites for acetone, but not for acetic acid. The time required to reach the equilibrium signal at this condition was only 8 - 20 min. The electrical response and t_{eqb} of the film to acetic acid was not affected by humidity.

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