Chapter 3

Polymer Weight Variations in Polymer/Carbon Black Chemiresistor Vapor Sensors

3.1 Abstract

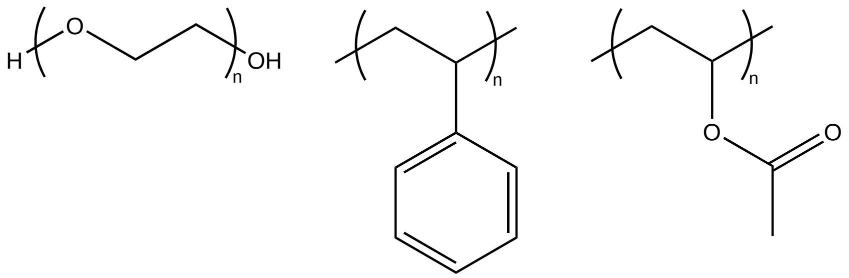
Broad molecular weight ranges of three polymers have been tested in polymer/carbon black composite chemiresistor sensors to determine if varying M_w alters or adds information to sensor response. The polymers studied — poly(ethylene oxide), poly(vinyl acetate), and polystyrene — span a wide range of glass transition temperatures (T_g). Sensor responses revealed that in the case of polystyrene, the high T_g polymer, response times were sharply decreased for the lowest M_w samples, increasing its practical use as a vapor sensor. Quartz crystal microbalance (QCM) measurements demonstrate that this decreased sensor response time is notably faster than the mass uptake response of the pure polymer.

3.2 Introduction

Conductive composites of carbon black mixed with thermoplastic polymers have attracted widespread interest over the last two decades for their uses as chemiresistive vapor sensors.[1–7] Films of such materials swell reversibly when exposed to an analyte vapor, yielding a change in the resistance of the sensor film.[8]

Responses of a given sensor vary with analyte, but are non-selective. Creating an array of such sensors each utilizing a different polymer yields response patterns allowing detection and quantification of a wide variety of analytes.[1,9] The selection of polymers for use in a sensor array depends on the intended use of the array. Similarities in polarity and functional groups between polymer and analyte are known to produce clear responses, and a broadly responsive array would incorporate polymers collectively containing a variety of functional groups.[10–12] Chiral polymers have been employed to differentiate between enantiomeric pairs of analyte vapors,[13]and reactivity between acidic and basic groups has been exploited to increase the overall sensitivity of an array.[14]

Less attention has been paid to the physical nature of the polymers used as the responsive chemical component in such arrays. A given polymer is assumed to have a glass transition temperature (T_g) below which the long-range motions of the polymer chains stop, and it assumes glassy, brittle qualities. Above T_g the polymer chains can slide past each other, and the bulk material becomes more flexible. Addition of plasticizer materials can significantly decrease the T_g of a polymer. The plasticizer molecules interpolate themselves between the polymer chains. This increases the average inter-chain separation and acts as an internal lubricant, allowing the chains to slide past one another more easily.[15]



poly(ethylene oxide) polystyrene poly(vinyl acetate)

Figure 3.1: Polymers used in these experiments

Composite chemical vapor sensors as described generally employ polymers with T_g well below the operating temperature of the system, as polymers with high T_g yield extremely slow response times.[3,4] To take advantage of its lubricating properties, a plasticizer material is added to the composite, yielding a tripartate mixture: carbon black, polymer, and plasticizer. Even in materials with low T_g, addition of plasticizer can decrease the sensor response time.

Molecular structure and polarity of a polymer affect T_g.[16] Rigid backbone units or bulky sidegroups all provide barriers to polymer chain motion, which raises T_g. Additionally, increasing polarity increases T_g, as interactions between polymer repeat units increase. As such, even with plasticization, many polymer structures have remained largely unavailable to use in composite chemiresistors, such as many polyamides, or polymers containing many phenylene groups (such as polystyrene).

T_g is not, however, the only attribute that contributes to the polymer response time. The ability of the analyte molecules to penetrate the sensor film also plays a role in this process. Very thick films yield slower response times. It has been proposed that lowered viscosity of the matrix polymer could aid in the diffusion of organic vapors through the film.[4] Viscosity of a given polymer increases with the molecular weight of the polymer, following the Mark-Houwink-Staudinger-Sakurada (MHSS) relation:

$$[\eta] = K\overline{M}_v^a \tag{3.1}$$

in which K is the MHSS "constant" and a the MHSS exponent. $\overline{M}_v$ is the viscosity average molecular mass. K and a both depend on the exact polymer-solvent pair, as well as the temperature. However, for a linear flexible polymer, a is generally between 0.5 and 0.8. The intrinsic viscosity (or limiting viscosity number) $[\eta]$ is expressed in units of reciprocal density.[16]

Studies have revealed a decrease in the percolation threshold (i.e., the percentage of conducting filler at which the mixture experiences an insulator-to-conductor transition) as the molecular weight of the polymer decreases.[17,18] Another study reports a mix of low and high molecular weight polyethylene (PE) in which the carbon black preferentially disperses into the low molecular weight regions of PE.[19] Polystyrene/CB composite materials prepared by in-situ polymerization showed increased responsivity and decreased response times for lower molecular weight polystyrene.[5] However, none of their sensor responses reached equilibrium status, the polydispersity indices (PDI) of their prepared polymers increased dramatically as molecular weight decreased, and they only covered a single order of magnitude range in the number average molecular weight (M_n) and a twofold variation in the weight average molecular weight (M_w). Most other studies of such sensors have been blind to the molecular weights of the polymers used.

Polymer	**T_g (°C)[16]**	**M_w Used**	**Reported $[\eta]$ Values (ml/g)**
PEO	-67	7.3x10^3–1.2x10^6	152–9330[a]
PVAc	35	1.5x10^4–5.0x10^5	12–189[b]
PS	98	2.5x10^3–2.0x10^6	16–189[c]

[a] Values for PEO M_w = 5k–2.2M, at 25 °C in H_2O.[20]
[b] Values for PVAc M_w = 11k–600k, at 30 °C in acetone.[21]
[c] Values for PS M_w = 38k–3.3M, at 35 °C in cyclohexane.[22]

Table 3.1: Physical characteristics of the polymers used in these experiments. M_w values are the weight average molecular weights of the polymers used. Reported $[\eta]$ (intrinsic viscosity) values are literature values determined for a weight range of each polymer as referenced.

It is clear that molecular weight affects the behaviors of carbon black/polymer composite sensors. In this study, three polymers (Figure 3.1, Table 3.1) spanning a range of T_g values have been explored as sensors, over a range of molecular weights, to determine if varied molecular weight alters or increases sensor responsiveness or sensitivity. The mass sorption and swelling properties of the listed polymers have also been examined via quartz crystal microbalance (QCM) and ellipsometry.

3.3 Experimental

3.3.1 Materials

Poly(ethylene glycol) / poly(ethylene oxide) (PEG/PEO) materials were purchased from Scientific Polymer Products, at the following molecular weights (M_w) and polydispersity indices (PDI, equal to M_w/M_n): M_w = 7290, PDI = 1.08 (PEG 8); M_w = 33,300, PDI = 1.02 (PEG 33); M_w = 100,400, PDI = 1.04 (PEO 100); M_w = 243,200, PDI = 1.04 (PEO 260); M_w = 609,700, PDI = 1.03 (PEO 600); and M_w = 1,020,000, PDI = 1.15 (PEO 1.2M).

Poly(vinyl acetate) (PVAc) was purchased at the approximate M_w of 15k, 100k, and 260k (PVAc 15, PVAc 100, and PVAc 260) from Scientific Polymer Products. PVAc of approximate M_w = 500k (PVAc 500) was purchased from Sigma-Aldrich. GPC determination showed PDI of 2.5–3.5 for all materials.

Polystyrene (PS) GPC powder standards were purchased from Sigma Aldrich, at the following M_w:M_w = 2460, PDI = 1.01 (PS 2k); M_w =13,200, PDI = 1.06 (PS 13); M_w = 44,000, (PS 44, no PDI listed); M_w =280,000, (PS 280, no PDI listed); M_w = 2,043,000, PDI = 1.02 (PS 2M).

Reagent grade hexane, heptane, chloroform, ethanol, isopropanol, ethyl acetate, acetone, and tetrahydrofuran were acquired from VWR. Chromium metal was purchased from RD Matthes and gold wire (0.25 mm diam., 99.9+%) from Sigma-Aldrich. Dioctyl phthalate (DOP) was also acquired from Sigma-Aldrich. Black Pearls 2000, a carbon black (CB) material, was donated by Cabot Co. (Billerica, MA). All materials were used as received.

3.3.2 Sample Preparation

Sensor substrate slides were prepared as previously described (Section 2.3.2). In brief, layers of chromium and gold were thermally evaporated onto cleaned microscope slides, with a masked section down the long center axis of the slide. After deposition, slides were cut into 0.5 cm x 2.5 cm samples to use for later sensor film deposition.

All sensors were deposited from solutions of a given polymer and DOP (a plasticizer), mixed with CB. The polymer and DOP were first dissolved, after which carbon black was added, and the entire mixture then sonicated for $>$30 min to disperse the CB particles. All materials were added to 20 mL of solvent (PEO in $CHCl_3$, and PVAc and PS in THF) in amounts totalling 200 mg of solid materials. Mixtures for all polymers were prepared at both 20 and 40 weight percent (wt%) of CB, and all had a 3:1 mass ratio of polymer:DOP — i.e., solutions were prepared of 40/120/40 and 80/90/30 mg respectively of CB/polymer/DOP. Solutions containing only 90 mg of polymer or 90/30 mg of polymer/DOP (but no CB) were also prepared.

Resistive sensors and QCM samples were prepared from the CB-containing mixtures. Pure polymer and polymer/DOP films were used for both QCM and ellipsometry measurements. Two mixtures were made of each CB-containing formulation. Two resistive sensors were made from each mixture. QCM films were prepared from both mixtures.

All samples were prepared as previously described (Section 2.3.2). In brief, sensor and QCM samples were deposited via airbrush onto sensor substrates or QCM crystals, respectively, and ellipsometry samples were deposited onto cleaned pieces of silicon wafer using a spin coater, in order to obtain smooth, homogenous films. The baseline frequency of each QCM crystal was noted prior to film deposition, and all QCM samples were placed in a vacuum desiccator for at least 2 h prior to use. The frequency shift effected by deposition of the sensor film was then recorded, prior to QCM response data collection.

3.3.3 Measurements and Data Analysis

3.3.3.1 Chemiresistive Sensors

An automated vapor generation and delivery system was used to deliver background air and analyte vapors to the array of chemiresistive detectors (Section 2.3.3.1). Resistances of all sensors were continuously monitored by and recorded to the controlling computer.

The sensor array was placed in a chamber made from PTFE and stainless steel that was connected via Teflon tubing to the vapor delivery system. The sensors were initially exposed to a 2.5 L min^{-1} flow of air for a period of time sufficient to stabilize the baseline resistance of the sensors. A single exposure to an analyte vapor consisted of a baseline period of oil-free air with a water content of 12 ppth, followed by exposure to analyte, followed by a further purge of air. For PEO samples, these time periods were 200/100/200 s. PVAc samples were exposed to 100/100/100 s baseline/exposure/purge times. PS samples were initially run with time periods of 100/100/100 s, which were later increased to 200/350/200 s.

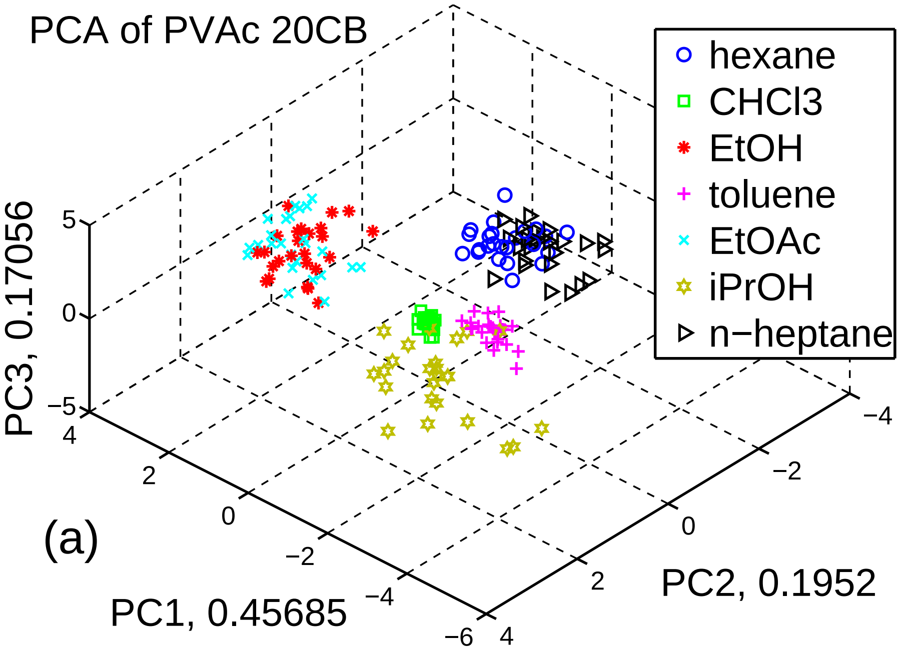
Analytes for all sensors were *n*-hexane, *n*-heptane, chloroform, ethanol, isopropanol, ethyl acetate, and toluene. In each sensor run, the seven analytes were presented in random order 25 times each to the detector array. All exposures were made at an analyte partial pressure ratio in air of $P/P^0 = 0.01$ (where P is the partial pressure and P^0 is the vapor pressure of the analyte at room temperature). Every sensor array was exposed to at least three sensor runs.

The resistance of each sensor was measured approximately every 5 s. The sensor response to each analyte is expressed as the relative change in resistance, $\Delta R_{\text{max}}/R_{\text{b}}$, where R_{b} is the steady-state baseline resistance of the sensor and ΔR_{max} is the maximum resistance change observed during exposure to the analyte. Signal-to-noise ratios (SNR) were also calculated for each exposure, with the SNR value defined as ΔR_{max} divided by the standard deviation of the data points used to calculate R_{b}. All values were calculated as previously reported (Section 2.3.3.1). Principal components analysis (PCA)[23] was performed on all sets of array data to visualize the analyte resolving ability of each array. All data analysis was undertaken in MATLAB.

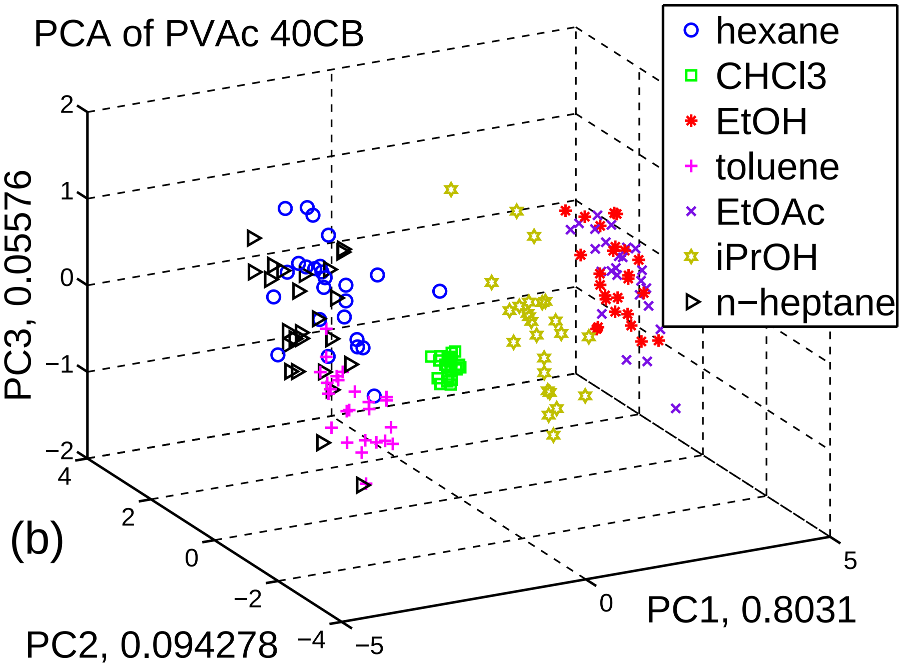
3.3.3.2 QCM Measurements

Coated QCM crystals were mounted in a chamber and exposed to analytes via a similar system to that used for the chemiresistive sensors (Section 2.3.3.2). Each crystal was exposed to baseline, analyte exposure, and purge steps. For all PEO films, these time periods were 100 s each. Mixed PVAc films were exposed to time periods comprising 60/70/80 s, while pure PVAc films were exposed for periods of 100/100/100 s. All mixed PS films were exposed for time periods of 100/150/100 s, and pure PS films, due to extreme slowness of response and purge time, were sampled with time periods of 300/600/300 s. Hexane and ethyl acetate were the analytes for QCM measurements, and were exposed to the QCM films at a partial pressure of $P/P^0 = 0.01$. The two analytes were presented in random order 10 times each. Two or more data runs were recorded for each crystal.

Deposition of the sensor film on the QCM crystal causes a change in frequency Δf_f, and each exposure to an analyte causes a further frequency shift, Δf_a. The ratio of the analyte shift to the film shift allows the determination of the mass absorbed per mass of the deposited film ($\Delta m_\mathrm{a}/m_\mathrm{f}$, a unitless quantity) via the use of the Sauerbrey equation (Section 2.3.3.2), which directly relates changes in mass and frequency of a thin film coated quartz crystal. The $\Delta m_\mathrm{a}/m_\mathrm{f}$ values for all exposures were then calculated and used for further QCM analysis.

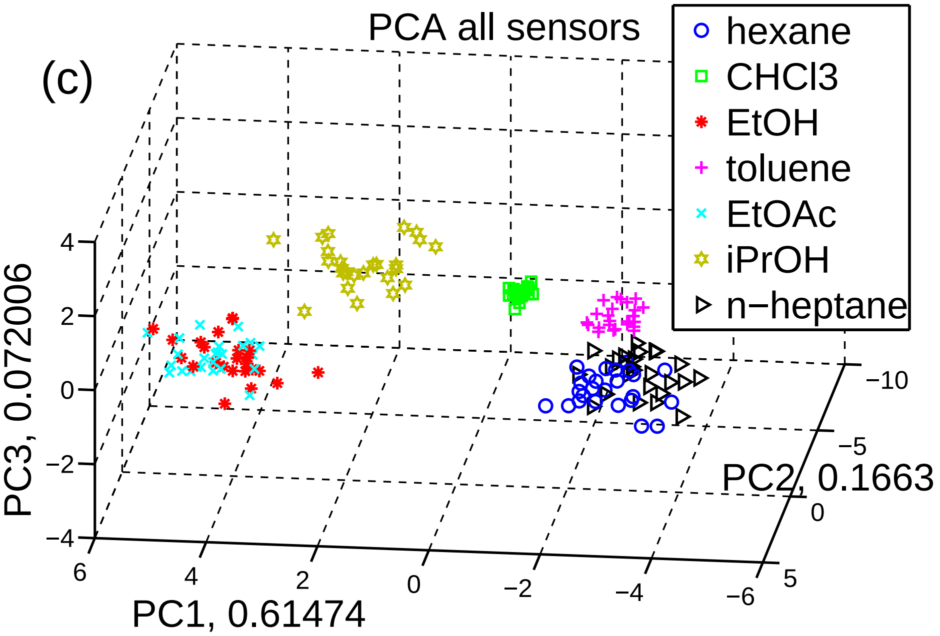


3.2(a) PCA plot PVAc 20 wt%



3.2(b) PCA plot PVAc 40 wt%

Figure 3.2: PCA plots of a) PVAc 20 wt%, b) PVAc 40 wt%, and c) both PVAc 20 and 40 wt% sensors. There are 25 exposures to each analyte. Numbers next to each principal component axis reflect the percentage of the total sensor response variance contained in that principal component (continued on next page).



3.2(c) PCA plot PVAc 20 and 40 wt%

Figure 3.2: (cont.) PCA plots of a) PVAc 20 wt%, b) PVAc 40 wt%, and c) both PVAc 20 and 40 wt% sensors. There are 25 exposures to each analyte. Numbers next to each principal component axis reflect the percentage of the total sensor response variance contained in that principal component.

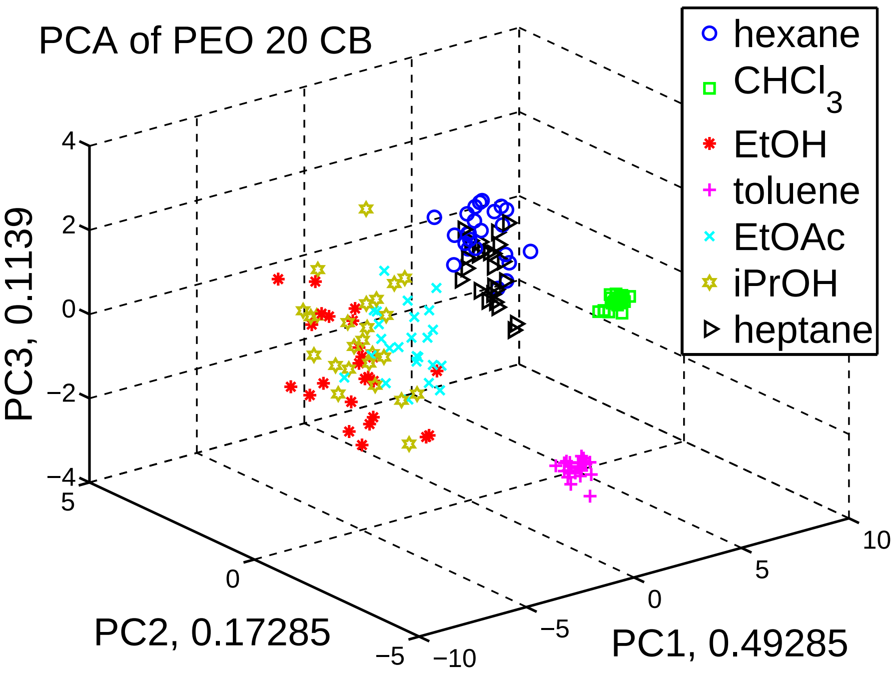


Figure 3.3: PCA plot of PEO 20 wt%. There are 25 exposures to each analyte. Numbers next to each principal component axis reflect the percentage of the total sensor response variance contained in that principal component

3.3.3.3 Ellipsometry

Ellipsometry was performed with a Gaertner L116C system. Samples for ellipsometry were placed in a plastic chamber with a drilled opening at each end to allow the laser beam to reach the sample and detector in an unobstructed fashion. Baseline thickness readings were collected under a steady 65 mL min^{-1} stream of air, with an adjacent ventilation tube used to flush the chamber. Exposures to saturated hexane vapor at 65 mL min^{-1} were initiated by hand. During the exposures, the ventilation tube was removed, to encourage maximum retention of hexane in the chamber. The purge and exposure times were each $\geq$5 min. Each sample was exposed a minimum of five times, and at least five data points were measured during and between each exposure. These data points were averaged to yield the relative thickness change of the film for each analyte exposure.

3.4 Results

3.4.1 Chemiresistive Sensors

All sensors responded to all analytes presented to the arrays. PEO sensors responded in an equilibrium fashion in the time periods investigated. PVAc sensors generally responded within the given time. PS sensors mostly did not achieve equilibrium resistance responses within either the 100 s or 350 s exposure periods. All sensors had highest $\Delta R/R_b$ values in response to $CHCl_3$ and toluene.

PCA plots of both PEO and PVAc sensor responses responses yielded separation between some analytes (non-equilibrium responses of PS are not suitable for PCA). Both

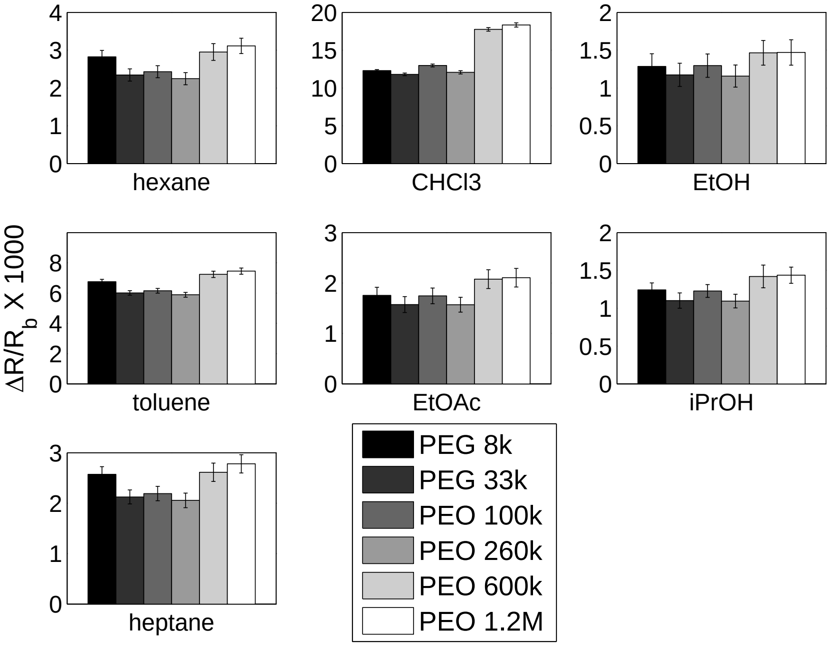


Figure 3.4: PEO (20 wt% CB) $\Delta R/R_b$ values in response to all seven analytes. Values are the average of 25 exposures to each analyte, and the error shown is one standard deviation.

polymers clearly separated chloroform and toluene from all other analytes, and separated the other polar analytes (EtOH, iPrOH, and EtOAc) from the alkanes (hexane and heptane). PEO arrays separated hexane from heptane, and provided partial separation betwen the polar analytes (Figure 3.3). PVAc provided no separation between the alkanes, and did not differentiate between EtOH and EtOAc, but did clearly separate iPrOH from them. PCA using responses from both 20 and 40 wt% PVAc sensors provided clearer separation than either PVAc 20 or PVAc 40 sensors by themselves (Figure 3.2).

All molecular weights of a given polymer displayed the same pattern of responses to the varied analytes. PVAc $\Delta R/R_b$ values were not entirely consistent across the M_w distribution, with $\Delta R/R_b$ values generally highest for PVAc 15. PEO displayed flat responses across all molecular weights to each analyte (Figure 3.4).

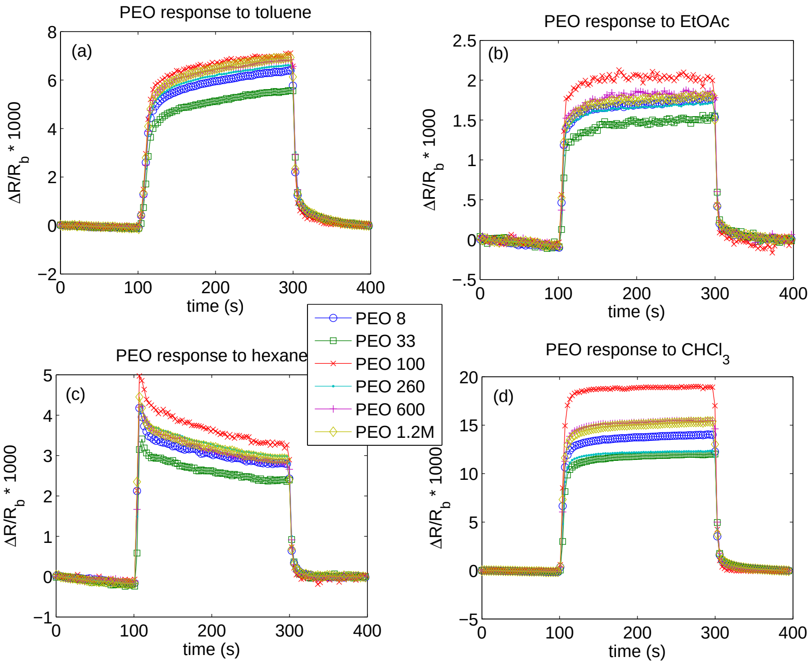


Figure 3.5: $\Delta R/R_b$ values of 200 second single exposures of PEO (20 wt% CB) to a) toluene, b) EtOAc, c) hexane, and d) $CHCl_3$. Each analyte was presented at $P/P^0 = 0.01$, in a total 2.5 L min^{-1} flow of air.

Single response curves of all weights of PEO displayed similar response times and curve shapes to all analytes (Figure 3.5). PS curves at both 100 s (Figure 3.6) and 350 s (Figure 3.7) exposure times showed a change in response as M_w of the polymer increased, showing quick equilibrium responses for PS 2k and PS 13, and much slower rise and fall times for all other molecular weights. At 350 s exposures, larger M_w polymers came to a greater percentage of the $\Delta R/R_b$ of the PS 2k/PS 13 response than during the 100 s exposures. They still did not achieve equilibrium during the longer exposure to any analyte other than chloroform, to which they displayed a stable response after about 200 s.

3.4.2 QCM Responses

All films displayed mass uptake responses. For all three polymers, $\Delta m_{\mathrm{a}}/m_{\mathrm{f}}$ for 40 wt% CB films were larger than for 20 wt% CB films. Responses for each polymer were larger for CB-containing films than for non-CB-containing films. Responses were generally flat across M_w ranges.

All PEO films responded in an equilibrium manner within their 100 s exposure period. PVAc films were generally noisy, with smaller responses than PEO films. PS films at 40 wt% CB came to an equilibrium response within the 150 s exposure time. PS 20 wt% films did not quite achieve equilibrium within this time period, although PS/plasticizer films not containing CB did equilibrate within that length of time. Pure PS films did not achieve equilibrium within a 600 s time period, other than the PS 2k film (Figures 3.8–3.11).

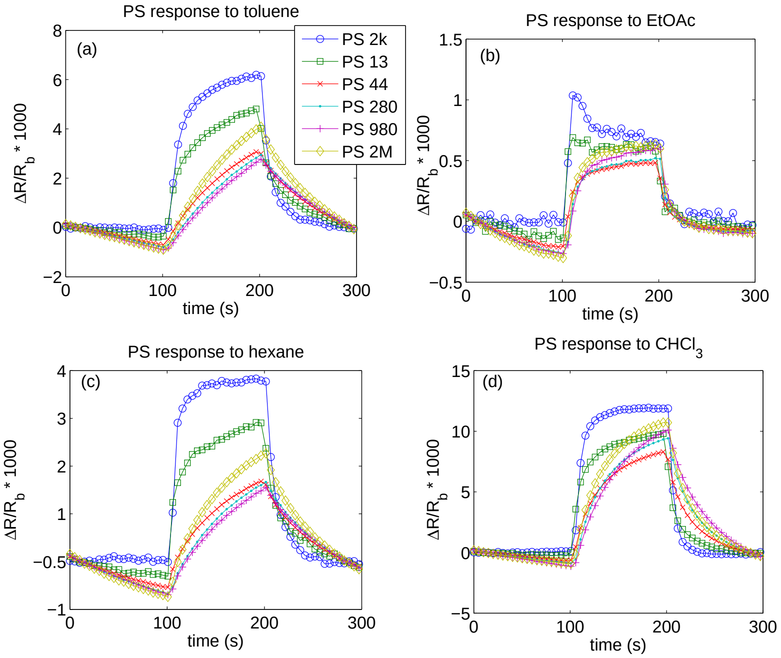


Figure 3.6: $\Delta R/R_b$ values of 100 second single exposures of PS (20 wt% CB) to a) toluene, b) EtOAc, c) hexane, and d) $CHCl_3$. Each analyte was presented at $P/P^0 = 0.01$, in a total 2.5 L min^{-1} flow of air.

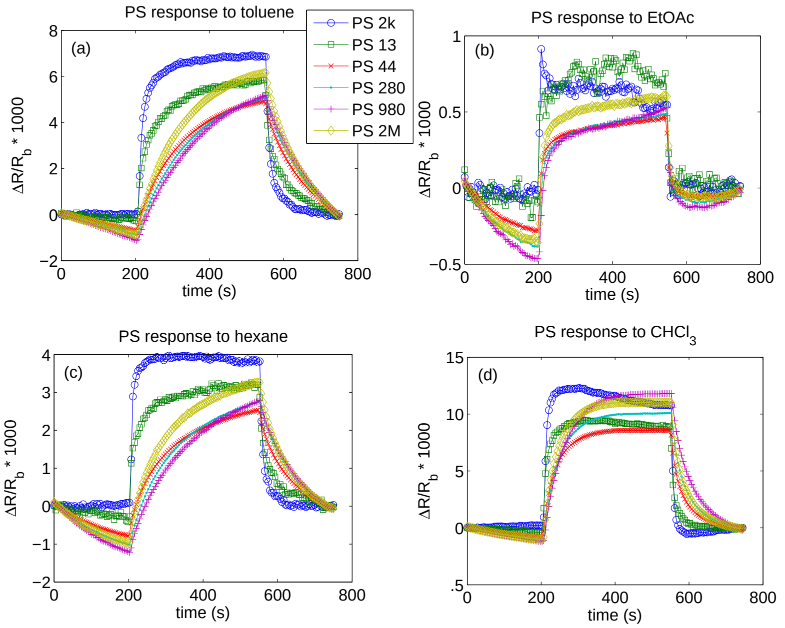


Figure 3.7: $\Delta R/R_b$ values of 350 second single exposures of PS (20 wt% CB) to a) toluene, b) EtOAc, c) hexane, and d) $CHCl_3$. Each analyte was presented at $P/P^0 = 0.01$, in a total 2.5 L min^{-1} flow of air.

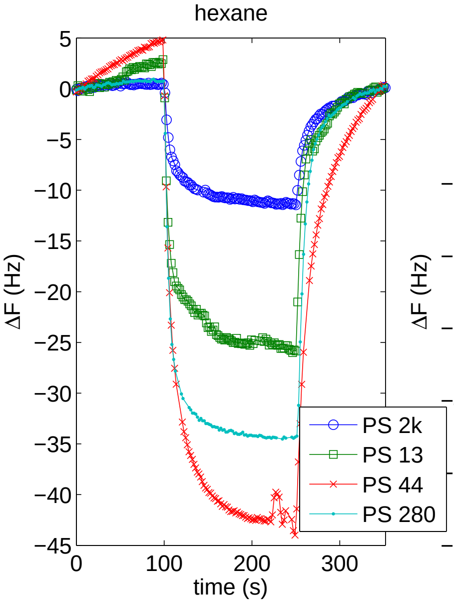


Figure 3.8: Single QCM responses of PS (40 wt% CB) films to hexane and EtOAc. Each analyte was presented at $P/P^0 = 0.01$, in a total flow 2.5 L min^{-1} of air. PS 980 and PS 2M films are not displayed as their absolute responses were very large, due to the thickness of those films.

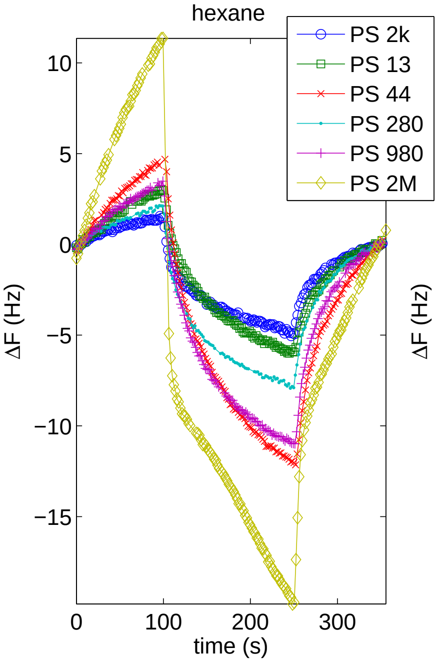


Figure 3.9: Single QCM responses of PS (20 wt% CB) films to hexane and EtOAc. Each analyte was presented at $P/P^0 = 0.01$, in a total flow 2.5 L min^{-1} of air.

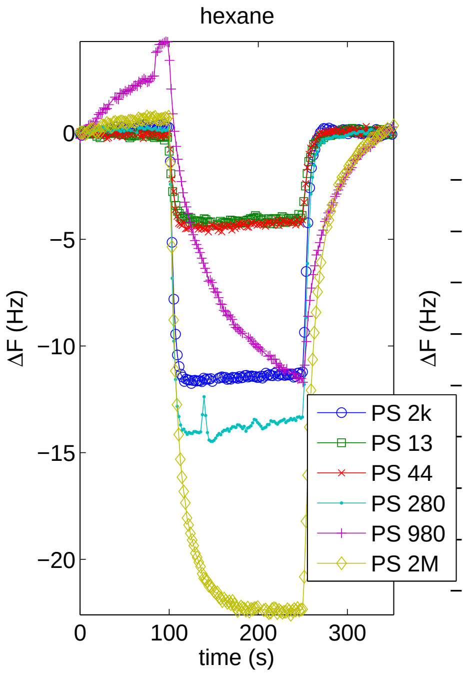


Figure 3.10: Single QCM responses of PS/plasticizer (3:1 ratio) films to hexane and EtOAc. Each analyte was presented at $P/P^0 = 0.01$, in a total flow 2.5 L min^{-1} of air.

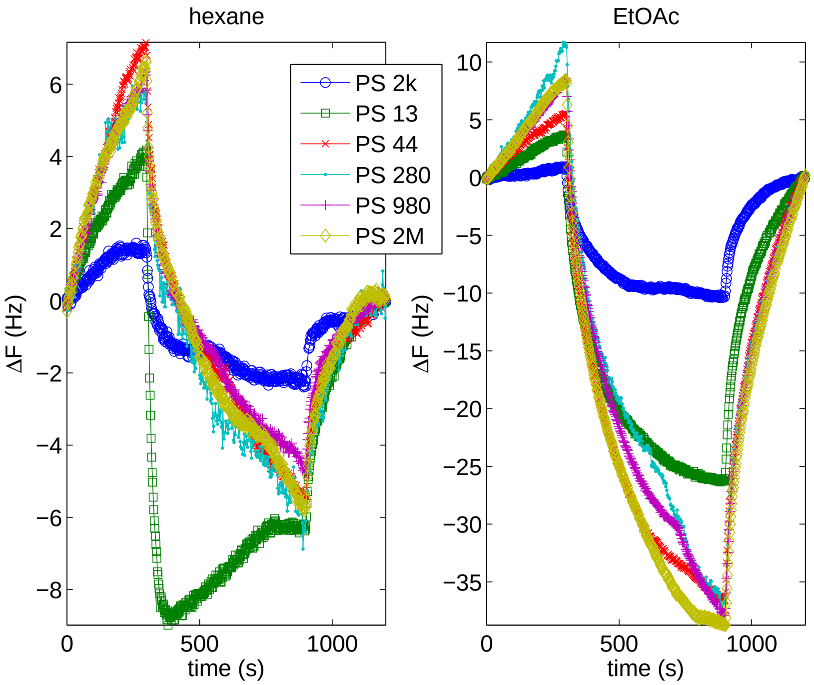


Figure 3.11: Single QCM responses of pure PS films to hexane and EtOAc. Each analyte was presented at $P/P^0 = 0.01$, in a total flow 2.5 L min^{-1} of air.

3.4.3 Ellipsometry

All polymer films responded to hexane vapor, showing stable responses after the 5 minute exposure period. Both pure polymer and polymer/plasticizer films displayed stable baseline thicknesses, with pure polymer films shifting $\leq$1% and polymer/plasticizer films shifting $\leq$2% of their original thicknesses over the course of the exposures.

Pure PEO and PVAc displayed swelling responses of $\sim$1.5–2% of their original thickness. Pure PS films swelled to a greater extent, around 6–7% in most cases (Table 3.2). Mixed polymer/plasticizer films were thicker than their respective pure polymer films, although deposition quantities were not rigorously controlled. Mixed films also swelled to a much greater extent than the pure films, usually from 8–12%. Responses were generally flat across the studied molecular weight ranges.

3.5 Discussion

High T_g polymers have largely been seen as unsuitable for use in polymer/carbon black composite chemiresistor sensors due to their extremely slow response times. These very long response times have been attributed to the swelling mechanism of such sensors being inhibited in their glassy state, below their T_g. Lower viscosity, however, can be seen as affecting both the ability of a polymer to swell, and the ability of an analyte vapor to penetrate a polymer matrix. Here use of arrays of monodisperse molecular weight polymers are seen to provide some discrimination ability. Additionally, very low M_w sensors of polystryene, a high T_g polymer, respond on a much reduced time scale, potentially opening the door to use of other high T_g sensors in composite sensors.

Polymer		**No DOP Plasticizer**		**With Plasticizer**	
		t (Å)	$\Delta h/h$ **(%)**	**t (Å)**	$\Delta h/h$ **(%)**
PEO	8	313	1.5(0.3)	381	10.3(0.5)
		330	1.7(0.3)	367	13.4(0.3)
	35	355	1.5(0.1)	402	18.8(0.8)
		363	1.3(0.1)	393	17.7(0.8)
	100	402	1.6(0.1)	461	10.8(1.0)
		399	1.9(0.2)	532	5.1(0.5)
	250	410	1.9(0.2)	627	11.4(0.5)
		428	1.3(0.2)	582	12.5(0.8)
	600	450	2.1(0.6)	698	7.1(0.3)
		446	1.9(0.3)	601	2.9(0.1)
	1.2M	574	1.8(0.3)	911	8.2(0.4)
		606	1.6(0.3)	889	8.3(1.0)
PVAc	15	367	2.1(0.1)	365	10.0(0.7)
		369	2.2(0.2)	380	7.6(1.3)
	100	363	1.6(0.2)	511	10.1(0.7)
		372	0.9(0.1)	497	10.3(0.3)
	260	372	1.4(0.3)	457	8.2(1.0)
		326	1.4(0.1)	434	16.3(1.0)
	500	354	1.7(0.4)	489	7.2(0.5)
		391	1.7(0.1)	428	12.5(0.5)
PS	2k	283	9.1(0.7)	570	10.9(0.5)
		337	8.5(0.7)	460	n/a
	13	285	6.7(0.5)	421	10.2(0.5)
		282	6.6(0.2)	417	9.0(0.3)
	44	303	7.1(0.6)	400	10.4(0.2)
		313	6.2(0.6)	395	9.9(0.6)
	280	377	6.8(0.6)	547	9.7(0.8)
		383	6.6(0.1)	518	10.6(0.4)
	980	339	7.3(0.2)	458	8.1(0.3)
		347	5.9(0.5)	612	11.4(0.4)
	2M	303	7.1(0.3)	704	11.2(1.1)
		349	6.8(0.2)	806	9.5(1.0)

Table 3.2: Averaged ellipsometry responses of PS, PVAc, and PS films to saturated hexane vapor at 65 mL min^{-1}. Reported error is one standard deviation. PS 2k film with no listed response began to break up during exposure.

3.5.1 Sensor Responses

Looking at $\Delta R/R_b$ values and single sensor responses yields valuable information about what does and does not change as the M_w of a given polymer is varied. Differing weight changes nothing about the chemical functionality of a polymer. As such, we see clearly that all tested M_w values show the same pattern of responses to the test suite of analytes. In Figure 3.4, all sensors have notably the largest response to chloroform, followed by their responses to toluene, with all other analytes eliciting smaller responses. The response pattern is presumed to be predicated on the chemical functionality of the polymer, and the pattern retention across M_w values provides further evidence of this.

In PEO, a sensor that achieves equilibrium resistance changes within tens of seconds (Figure 3.5), it is also seen that M_w does not change the $\Delta R/R_b$ values reached (Figure 3.4). This flat response indicated that in systems already reaching rapid equilibrium (e.g., low T_g polymer composites) viscosity variations do not alter the ability to achieve an equilibrium response.

In a high T_g polymer such as polystyrene, however, we can see a substantial decrease in response time attributable to viscosity differences. The lowest weights of PS tested, PS 2k and PS 13, achieved an equilibrium response within a time period similar to that of PEO, tens of seconds. Higher M_w PS polymers generally did not reach stable $\Delta R/R_b$ responses in 100 s for any analyte (Figure 3.6), and not in over five minutes of exposure time for non-polar analytes (Figure 3.7). Time for resistance recovery to baseline also greatly decreased in the low M_w PS sensors, indicating that both adsorption and desorption processes are affected.

In the case of polystyrene, T_g does drop as M_w values get very low. The changes in T_g have been experimentally determined to follow the Kanig-Ueberreiter equation, Eq. (3.2):[24,25]

$$\frac{1}{T_g(M_n)} = \frac{1}{T_g(\infty)} + \frac{K}{M_n} \tag{3.2}$$

with K = 0.78, and the asymptotic value of T_g = 371 K (98 °C). Even at the low weight limit of PS 2k, however, with reported M_n = 2440, the T_g = 61 °C, still well above the operating temperature of the sensors. PS 13, with reported M_n = 12,400, has T_g = 92 °C, very close to the limiting value. While dioctyl phthalate as a plasticizer does lower the T_g values of polystyrene,[26] the difference in baseline T_g between PS 13 and the higher M_w polystyrenes is insufficient to allow plasticization of the molecule to solely explain the disparities in their response curves.

Both of the quickly responsive molecular weights of PS are also below the critical molecular weight (M_c) of polystyrene of around 31,000 (M_c for PVAc is around 24,000 and for PEO is under 5,000. All PEO weights used were above this, and the PVAc samples used were all high PDI).[27] M_c is the weight above which the polymer molecules have sufficient length to intertwine, and the dependence of the zero shear rate viscosity versus log of molecular weight enters a different power regime. This weight directly references a quality of the pure polymer, whereas the intrinsic viscosity relates to the ability of a polymer to affect a mixed solution viscosity. Entanglement molecular weight is often used in discussion of high temperature pure polymer melts and solids, and it is difficult to assess how it reflects on composite sensor materials.

Lowered viscosity due to molecular weight, lack of entanglement, and potential plasticization all allow the lower M_w polystyrene samples to respond much more quickly as composite vapor sensors. Low molecular weight fractions of other high T_g polymers could also display these same improvements.

3.5.2 Array Discrimination

Both PEO and PVAc sensor arrays were able to provide some discriminatory power between analytes (Figures 3.3 and 3.2). A simple examination of the $\Delta R/R_b$ values for PEO (Figure 3.4) shows much larger responses for chloroform and toluene than for the other analytes. However, the simple $\Delta R/R_b$ responses to hexane are not notably different than those in response to EtOH or EtOAc, yet hexane is clearly separated from those in PCA plots, and clustered with heptane.

Enough information is clearly being captured across the sensor responses to make that separation. PVAc had a similar pattern of responses to PEO, and also showed separation along more than one axis of variance. Examination of the PCA plot for the PVAc 40 wt% CB sensors does reveal most separation along the first principal component, capturing 80% of the total variance returned by the sensors (Figure 3.2b). But the plots for PEO 20 wt% CB and PVAc 20 wt% CB have less than 50% of their total variance within the first PC, revealing a broader set of information being captured.

However, each analyte array contained multiple sensors of each molecular weight, thus increasing the overall number of inputs to PCA. We would expect very poor or no discrimination between analytes (and not along more than one dimension) if all sensors in the array were functionally identical. While this may indicate added resolving power afforded by molecule weight variation, it is not possible to completely disentangle that contribution from the variation added by having multiple copies of each sensor — deposition differences between each film could be a confounding source of added variation. The added clustering provided by the merging of the sensor response from both PVAc 20 and 40 wt% CB indicates how an induced difference of a physical nature can add variation (even as it showcases a simple way to increase sensor variety while including absolutely minimal chemical variation among a set of sensors).

3.5.3 Mass Uptake and Swelling

Pure PS films are very slow to sorb mass during QCM exposures, as PS in its glassy state below T_g is not highly permeable. Only PS 2k comes to an equilibrium response within the full 10 minutes of analyte exposure, although, as with the sensor responses, PS 13 comes close (Figure 3.11). This further supports these M_w levels being beneath some limiting mass that renders them more rapidly responsive, though they are still slow at mass uptake.

Mixed PS/plasticizer films, however, showed an enormous decrease in mass sorption times, with almost all mixed films coming to equilibrium within one minute. While this does not directly address changes in swelling time, it does indicate that plasticizer aids all M_w samples equally in pure mass sorption. It further demonstrates the difference between mass sorption and sensor response, as does the fact that all QCM films showed greater response to EtOAc than to hexane, the reverse of which held true with the chemiresistors.

Addition of carbon black to QCM films slowed down mass uptake compared to the polymer/plasticizer films. The CB-containing films were still notably faster than the pure polymer films. Unlike the sensor responses, or the pure polymer QCM films, no real response time differences related to M_w were seen, indicating the role of CB in mass sorption, and, again, highlighting the importance of both sorption and swelling in the responsiveness of these composite films.

When examined by ellipsometry, pure films of PS displayed much greater swelling in response to hexane than did films of PEO or PVAc, even with the relatively short exposure times (5 min.) compared to the response time scales seen with sensors and QCM films. As seen in Figures 3.4–3.7, the $\Delta R/R_b$ responses to hexane of the plasticized 20 wt% CB films of PEO and PS are similar in scale. However, the notable swelling of the PS film emphasizes the potential use of PS, a material not previously considered a good sensor candidate, due to its high T_g.

3.6 Conclusions

Polymer/CB sensor arrays comprised of only a single polymer substrate, but encompassing several molecular weights of that polymer, have been studied to examine the effect of M_w on sensor and array response. There is some evidence that the M_w variations are sufficient to provide analyte separation. Also, examination of low M_w polystyrene samples showed much improved sensor response times. As polystyrene and other high T_g polymers have generally been considered unsuitable for use in composite chemical vapor sensors, these data provide a path toward incorporating many other high T_g polymers previously considered inaccessible.

3.7 Bibliography

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