

Supporting information

for

AgBF₄-Impregnated Poly(vinyl phenyl ketone): An Ethylene Sensing Film

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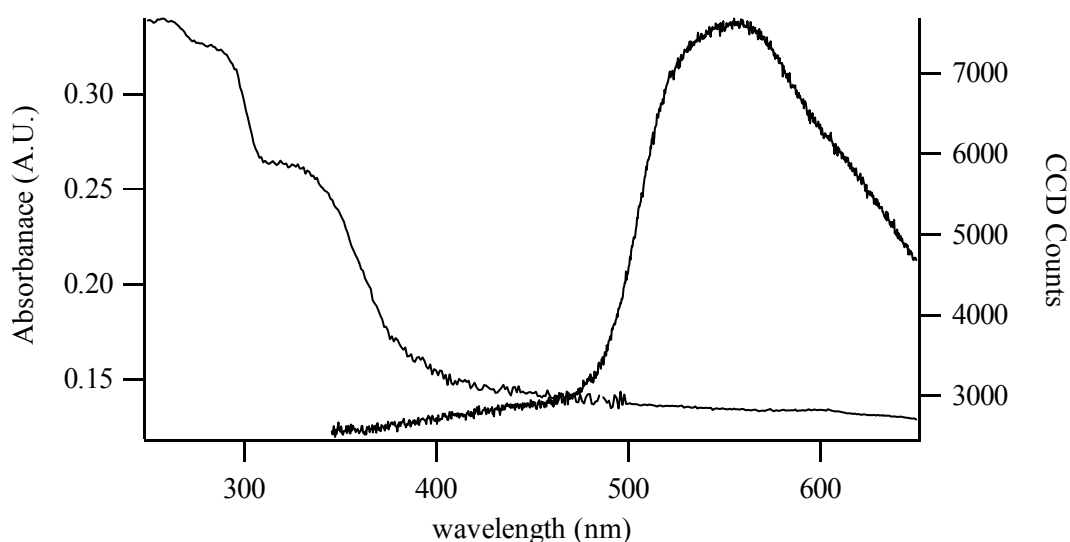


Figure s1a. Absorption (left) and emission (right) spectra of a 2:1AgBF₄:PVPK film. The transmission absorption spectrum of a CH₃CN-cast film on a quartz slide was collected with a Cary-4-Bio absorption spectrophotometer. The emission spectrum was collected upon excitation with 0.3 mW of 488 nm light from a Coherent Innova 90-4C Ar ion laser. Emission was monitored with an Oriel Multispec 77400 CCD detector via a fiber optic probe. For PL experiments, the film was excited at 488 nm to avoid polymer photodegradation, which has been reported to occur upon excitation at 366 nm (David, C.; Demarteau, W.; Geuskens, G. *Polymer*, **1967**, 8, 497-502).

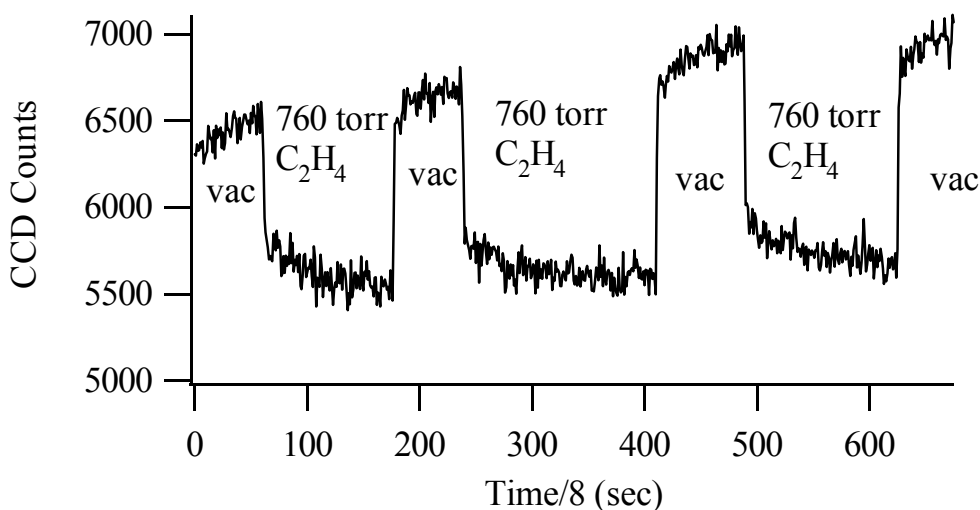


Figure s1b. Conditioning of the 2:1 film used to generate Figure 1. Shown is the PL response of the film during three cycles of conditioning, demonstrating the reversible response to 760 torr ethylene. The response was monitored at the emission maximum (575 nm). The baseline (vacuum) emission intensity increases during the conditioning process; the data for Figure 1 was collected once a stable baseline intensity was attained.

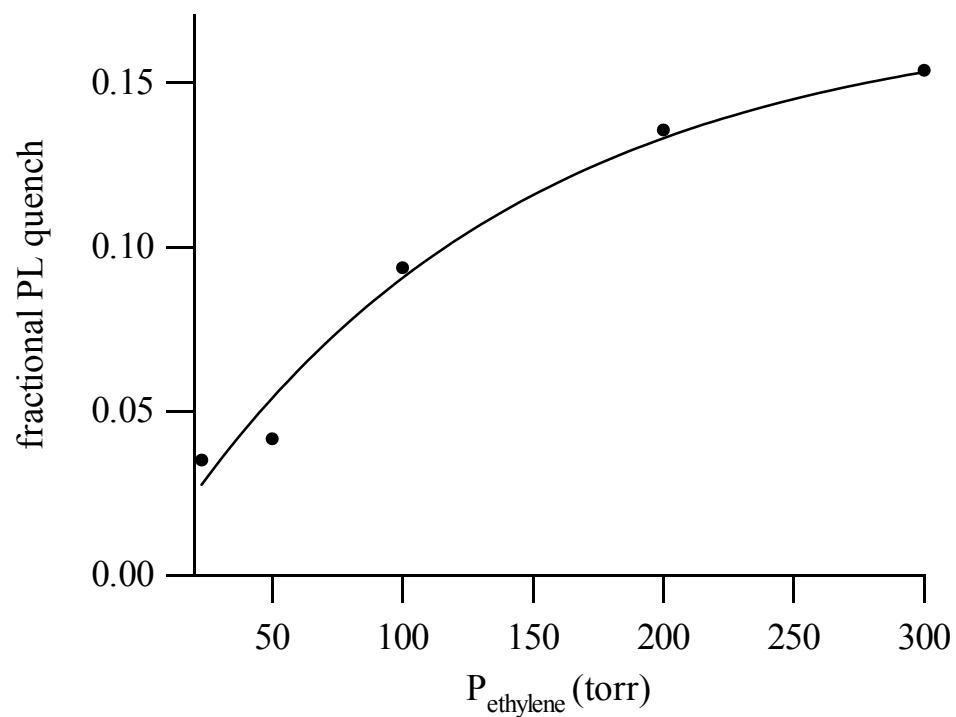


Figure s1c. Response curve for the experiment shown in Figure 1. The fractional PL quenching is plotted against the pressure of ethylene. Fractional quenching was calculated using the following equation:

$$\text{Frac. PL quench} = (\text{avg. CCD counts}_{\text{vac}} - \text{avg. CCD counts}_{\text{C}_2\text{H}_4}) / \text{avg. CCD counts}_{\text{vac}}$$

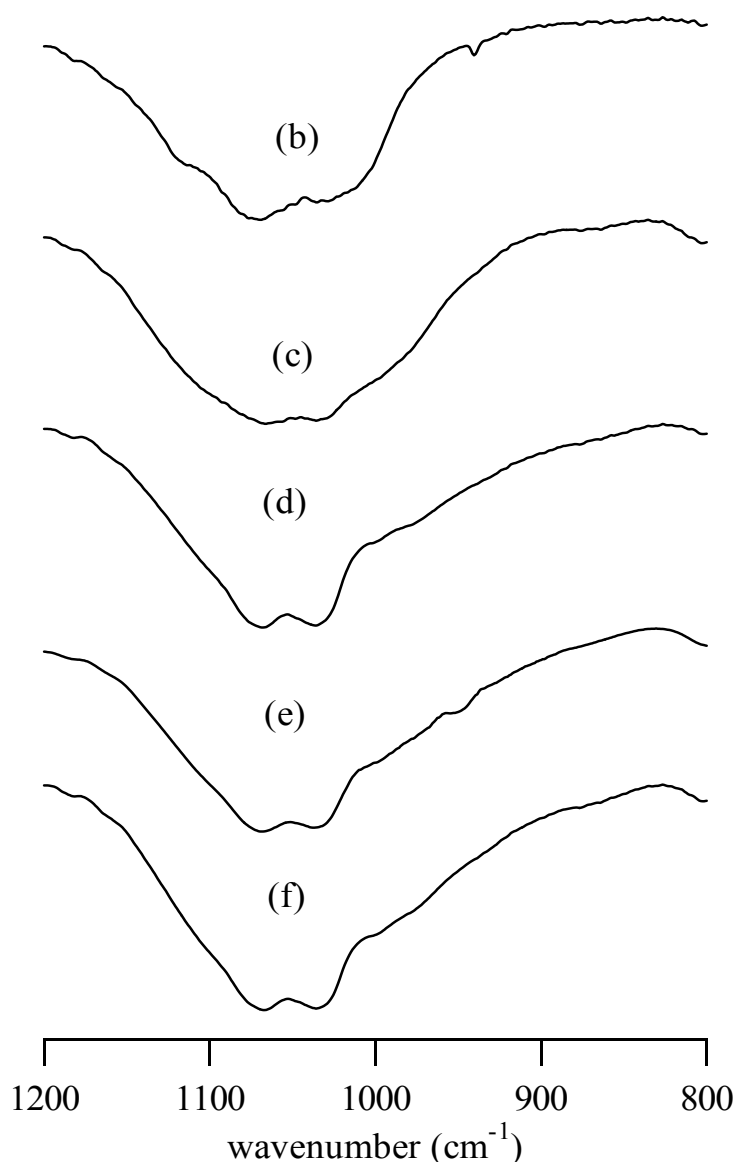


Figure s2. The ν_3 mode of the BF_4^- anion from the IR experiment shown in Figure 3 (Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; 4th Ed., John Wiley & Sons: New York, 1986). The spectra shown correspond to conditions (b), (c), (d), (e) and (f) of Figure 3. (b) 2:1 AgBF_4 :PVPK film as cast from CH_3CN , (c) film after one conditioning cycle, (d) film after six conditioning cycles, (e) film after exposure to 1 atm ethylene (under Ar), (f) film after exposure to 1 atm ethylene (under vacuum). Pure AgBF_4 exhibits an asymmetric, broad resonance centered at 1064 cm^{-1} with a single minimum (Horn, E.; Snow, M.R.; Tiekink, E.R.T. *Aust. J. Chem.*, **1987**, 40(4), 761-765). The freshly cast film exhibits three minima in the ν_3 mode, indicative of a low symmetry environment for the anion. After conditioning, two distinct minima in the ν_3 mode are observed, suggesting that the anion environment changes with the conditioning process. The ν_3 mode does not change upon ethylene binding, suggesting that the polymer-anion interactions remain constant.

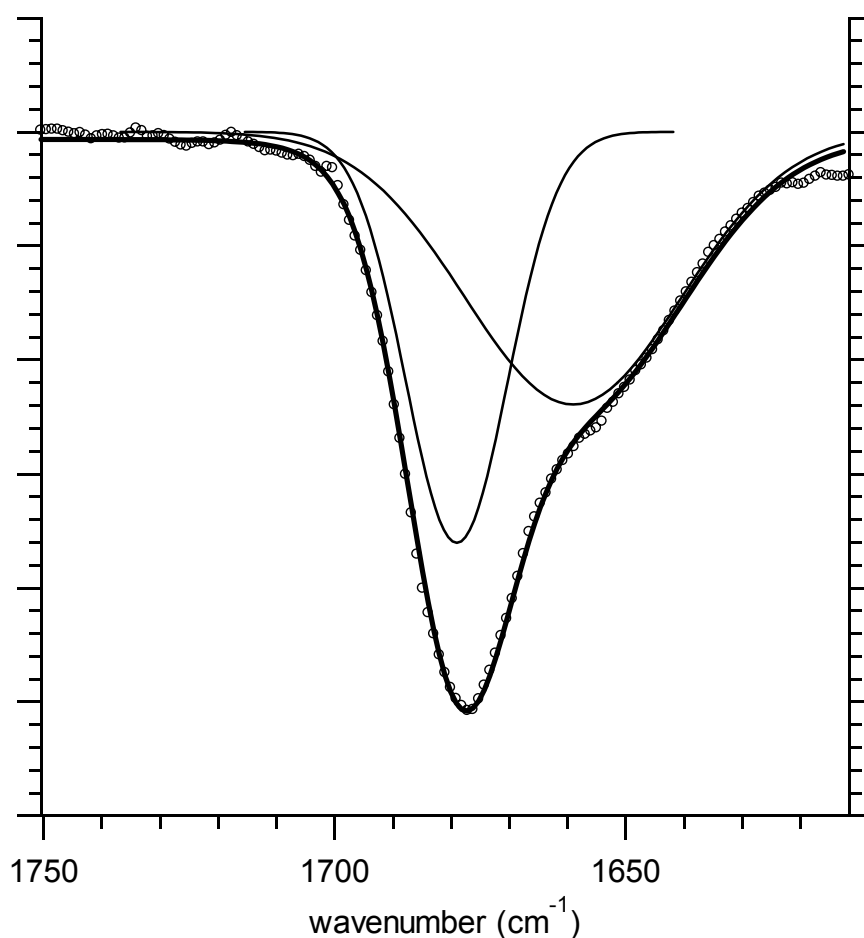


Figure s3a. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3b, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. Two Gaussian curves, obtained from fits of control spectra, were used to fit the data: one for free carbonyl (1680 cm^{-1}) and one for Ag^+ -coordinated carbonyl (1658 cm^{-1}). The intensities of the two contributing peaks were varied to optimize the fit. The width of the Ag^+ -coordinated carbonyl peak was allowed to vary and the width of the free carbonyl peak was fixed. This fitting procedure was also used to generate Figures s3b-f. The $\nu_{\text{C=O}}$ mode of pure PVPK was used as the model for the uncoordinated carbonyl and the $\nu_{\text{C=O}}$ mode of PVPK in the presence of 3 equivalents of AgBF_4 was used to model the Ag^+ -coordinated carbonyl. The percentage contribution of the free and Ag^+ -coordinated carbonyls are tabulated in table S1.

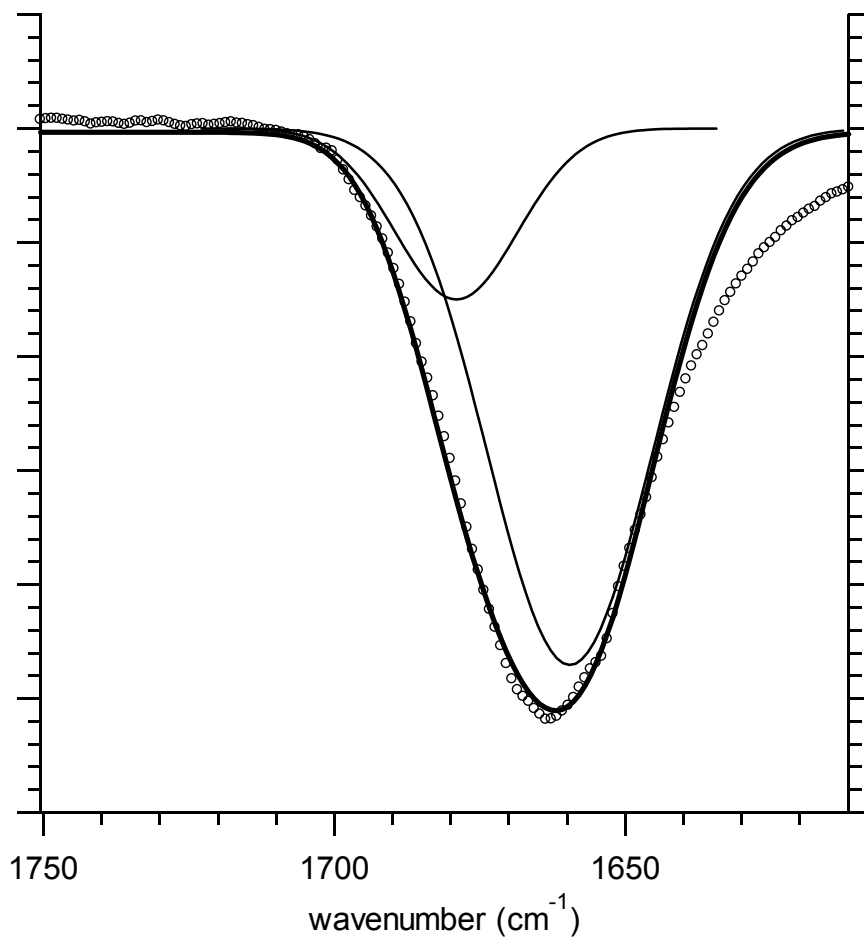


Figure s3b. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3c, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. The fit was obtained as described in Figure s3a.

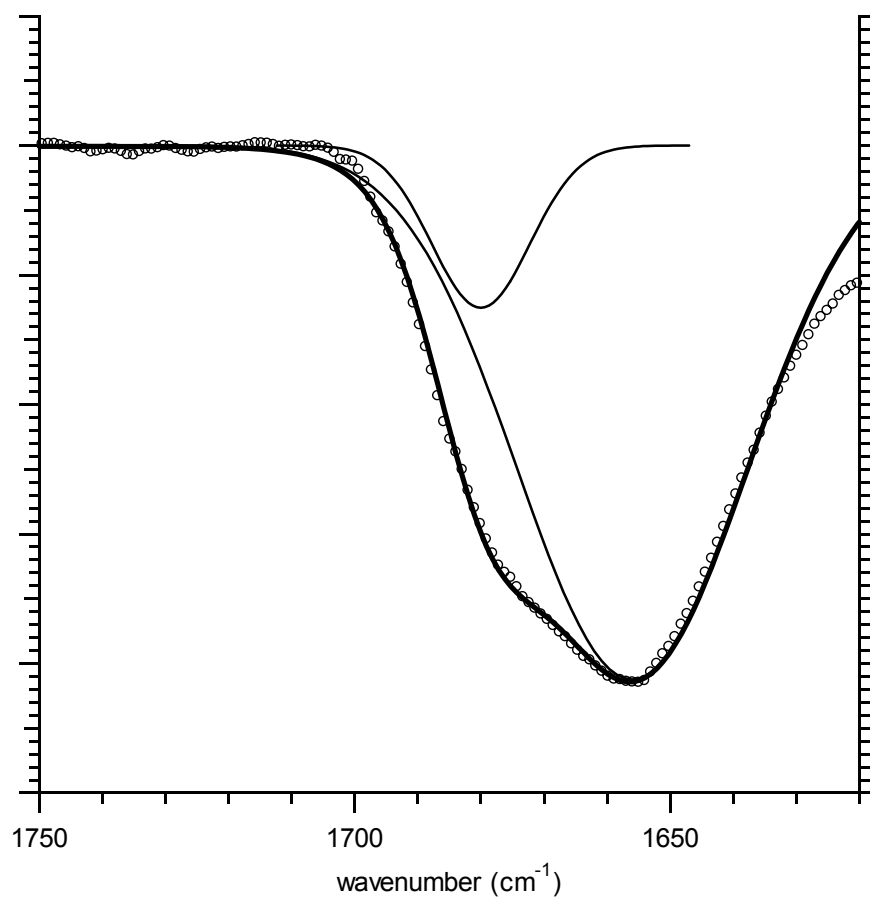


Figure s3c. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3d, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. The fit was obtained as described in Figure s3a.

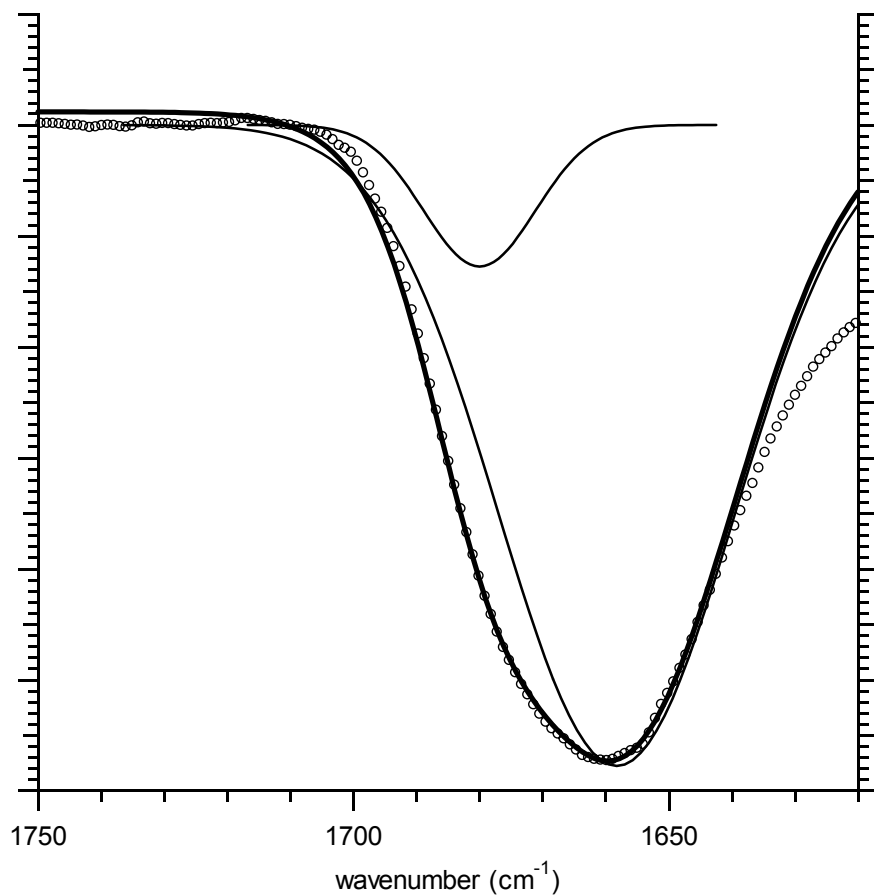


Figure s3d. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3e, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. The fit was obtained as described in Figure s3a.

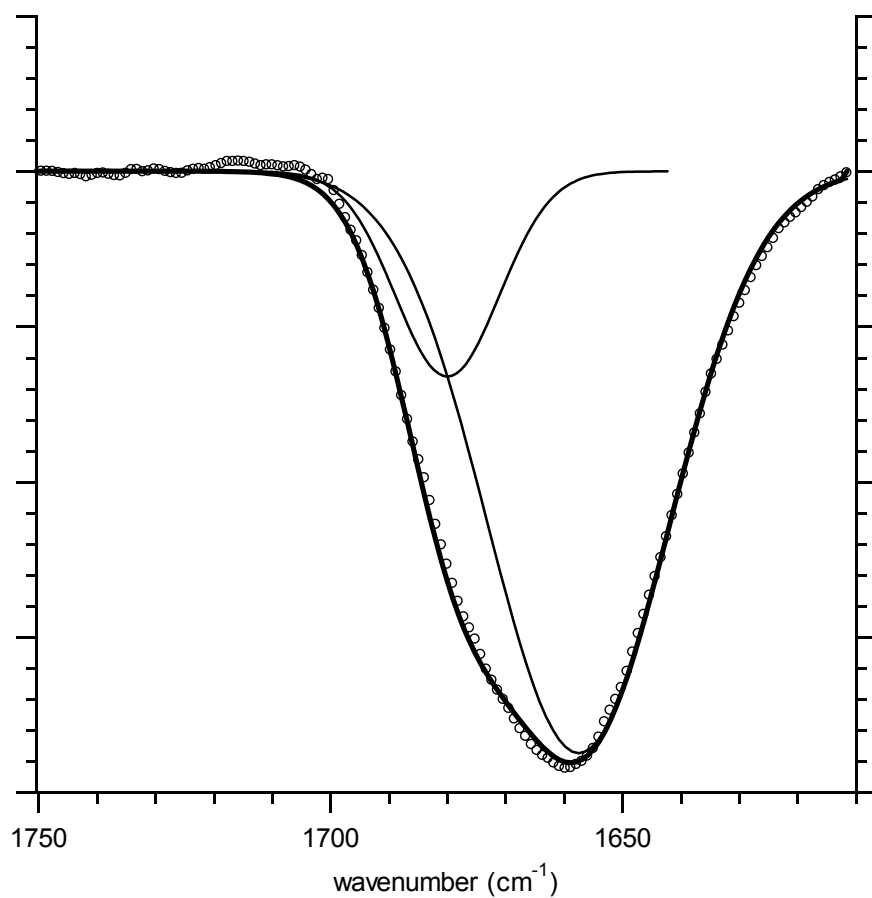


Figure s3e. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3f, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. The fit was obtained as described in Figure s3a.

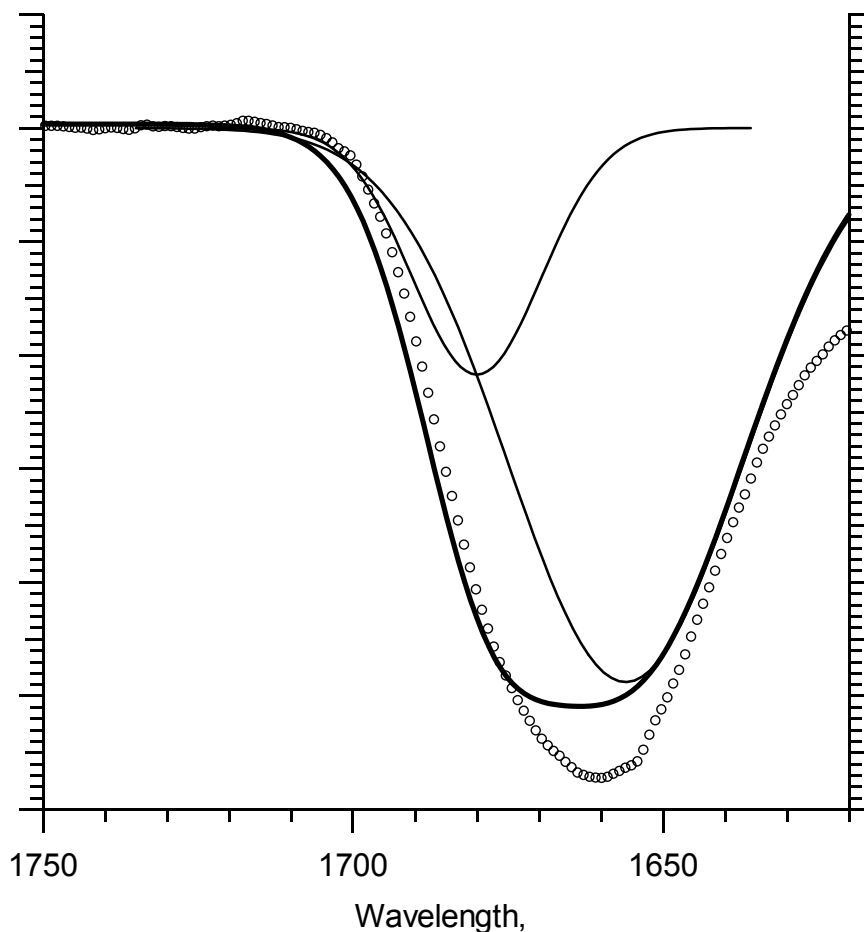


Figure s3f. The $\nu_{\text{C=O}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3e (open circles) plotted with a modeled spectrum (dark solid line). The model assumed that 20% of the carbonyl groups were displaced from within the Ag^+ coordination sphere upon binding ethylene, i.e. there was a 20% shift from bound to free carbonyl groups. The model was obtained as described in Figure s3a, with the intensities of the two bands scaled appropriately based on the control spectra. From the poor fit of the model we conclude that if 20% of the carbonyl groups in the polymer were displaced from the Ag^+ ions by ethylene, we would see greater asymmetry in the carbonyl resonance. We therefore conclude that either: 1) the accessible 20% of the sites quenched by ethylene are not quenched due to loss of coordinated carbonyl, or 2) the accessible 20% of the sites represent a very small minority of the bulk material whose IR spectra we observe, and the bulk sites do not lose coordinated carbonyl.

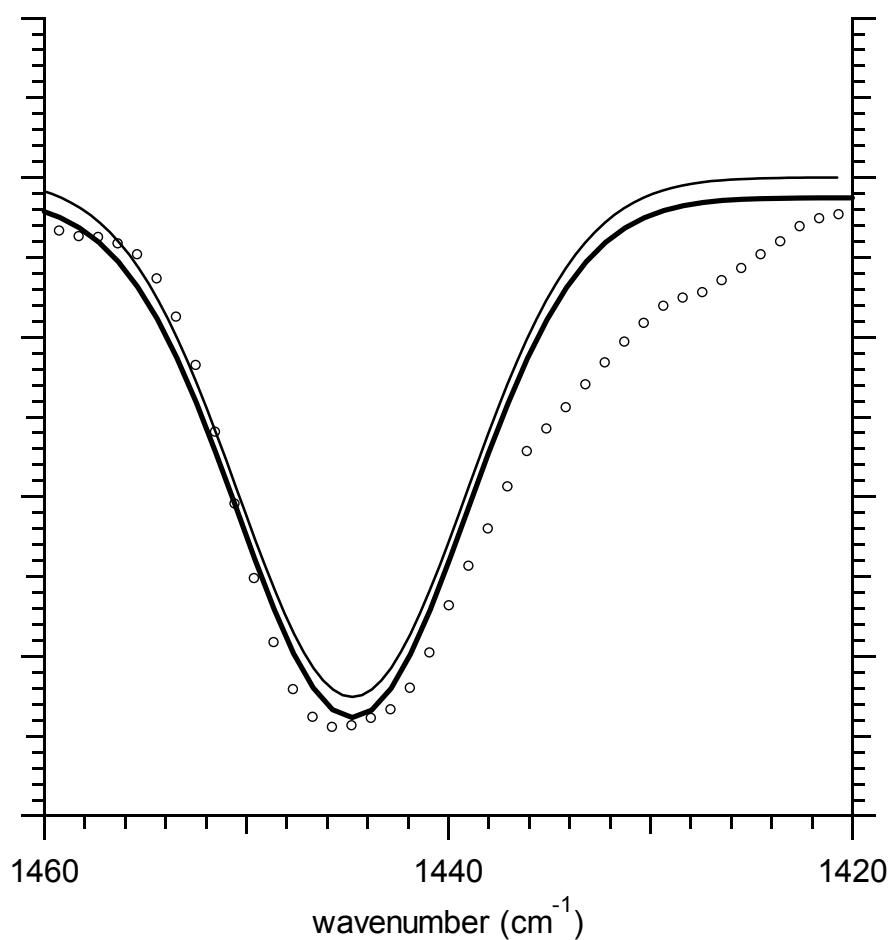


Figure s4a. The $\nu_{\text{C}=\text{C}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3d, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. One Gaussian curve, obtained from a fit of the $\nu_{\text{C}=\text{C}}$ mode of pure PVPK (1444 cm^{-1}), was used to model the data. The position of the peak was fixed and the width of the peak was allowed to vary. The same procedure was used to generate Figures s4b-c. The peak widths obtained from the fits are listed in Table s2.

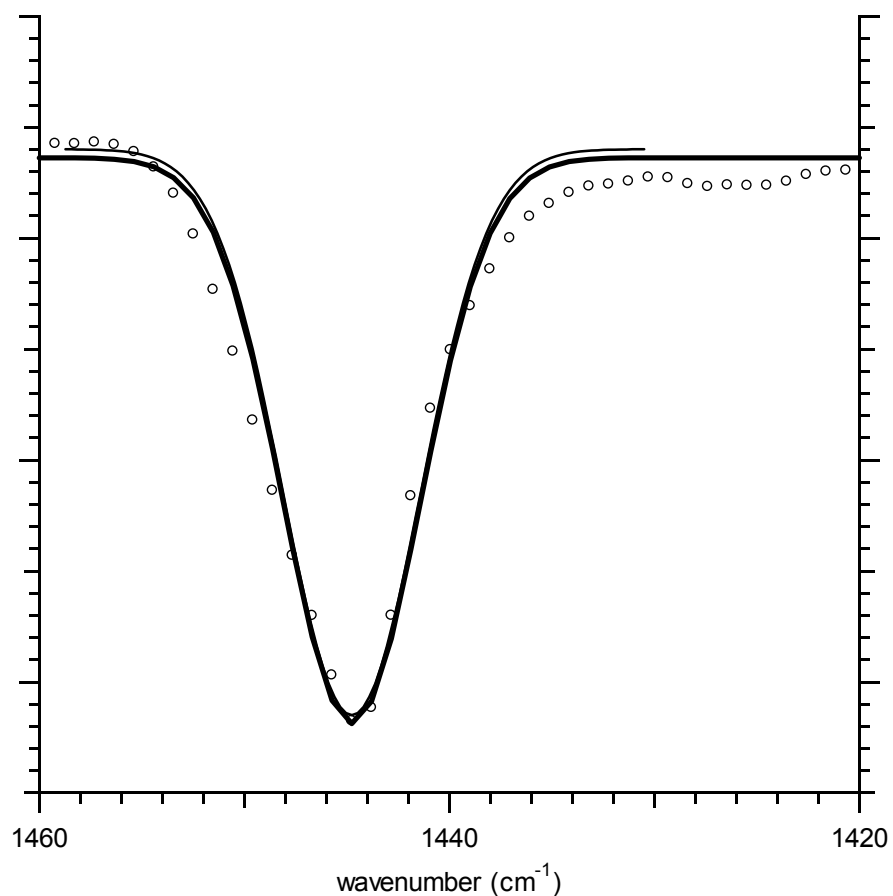


Figure s4b. The $\nu_{\text{C}=\text{C}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3e, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. This peak is comparable in width to that of pure PVPK, and narrower than that in Figures s4a and s4c, suggesting a reduction in the interaction of the metal center with the phenyl moiety upon exposure to ethylene. The peak widths obtained from the fits are listed in Table s2.

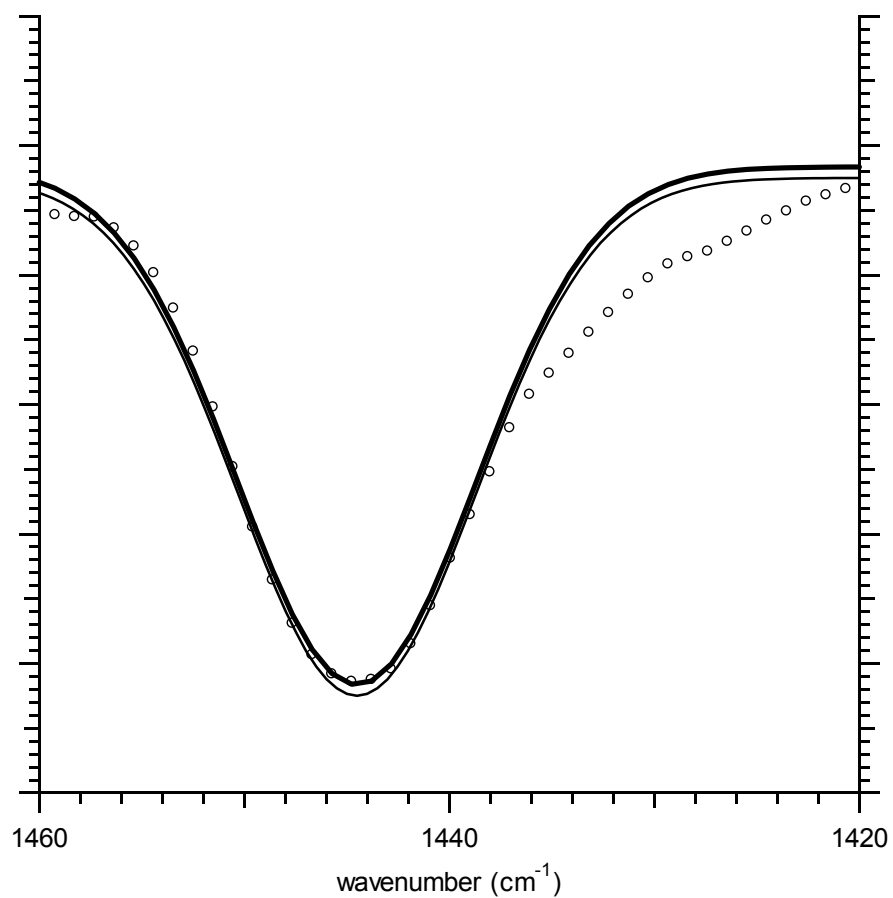


Figure s4c. The $\nu_{\text{C}=\text{C}}$ mode of 2:1 AgBF_4 :PVPK from Figure 3f, with line of best fit. The data are plotted with open circles and the best fit line is plotted with a dark solid line. This peak is of comparable width to that of Figure s4a, and is wider than that of Figure s4b. The peak widths obtained from the fits are listed in Table s2.

Table S1. Calculated contributions of $\nu_{C=O}$ bound and $\nu_{C=O}$ free to $\nu_{C=O}$ observed

	cm^{-1}	% contribution	% contribution (scaled) ^b
3b	1680	41.5	45.6
	1658	58.5	54.4
3d	1680	9.6	10.6
	1656	90.4	89.4
3e	1680	10.8	11.9
	1656	89.2	88.1
3f	1680	16.8	18.4
	1656	83.2	81.6

^a The percentage contributions to observed $\nu_{C=O}$ (Figures 3b-f) were calculated from the integrated areas of the Gaussian curves fit to $\nu_{C=O}$ as described in Figure s3a. The percentage of free $\nu_{C=O}$ was calculated using the following equation:

$$\% \nu_{C=O} \text{ free} = [(\text{Intensity } \nu_{C=O} \text{ free}) / (\text{Intensity } \nu_{C=O} \text{ free} + \text{Intensity } \nu_{C=O} \text{ bound})] \times 100$$

Since this model assumes two states (bound and free $\nu_{C=O}$), the percentage of bound $\nu_{C=O}$ was determined by subtracting this percentage from 100.

^b To account for differences in oscillator strength of bound and free $\nu_{C=O}$, spectra of 50 μL of THF solutions (5 mL) containing PVPK (35 mg) and PVPK (35 mg) metallated with AgBF_4 (150 mg) in a 3:1 molar ratio of AgBF_4 to PVPK functional groups, were compared. At the 3:1 ratio, the carbonyl resonance was fit by a single Gaussian which represented only bound carbonyl moieties. The ratio of the integrations of the bound and free $\nu_{C=O}$ revealed a scaling factor of 1.1, which was applied to the percentage free $\nu_{C=O}$ to account for the difference in oscillator strength. The scaled percentage of bound $\nu_{C=O}$ was determined by subtracting this percentage from 100.

Table S2. Calculated FWHM of $\nu_{C=C}$ at 1444 cm^{-1}

	cm^{-1}	FWHM (cm^{-1}) ^a
3d	1444	11.24
3e	1444	8.29
3f	1444	13.74

^a Full Width at Half Maximum Amplitude (FWHM) was calculated after a single Gaussian curve had been fit to the $\nu_{C=C}$ observed at 1444 cm^{-1} in Figures 3d-f as described in Figure s4a.