

# High-Pressure FTIR Studies of Gas–Polymer Interactions

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## Synopsis

FTIR spectra of cellulose acetate (CA) and poly(methyl methacrylate) (PMMA) at 35°C have been obtained as a function of carbon dioxide pressure at pressures up to 55 atm in a specially designed FTIR cell. Results indicate that the carbonyl stretching vibrations for CA (1752  $\text{cm}^{-1}$ ) and PMMA (1731  $\text{cm}^{-1}$ ) shift to slightly higher wave numbers with increasing pressure. The small shifts suggest dipole–dipole interactions between  $\text{CO}_2$  and the carbonyl group. In both cases, the shift appears to be linear with pressure. This linearity is interpreted in the framework of the dual-mode theory to suggest that gas–polymer interactions occur in the Henry's law dissolution mode.

## INTRODUCTION

Gas separations represent important applications for synthetic polymeric membranes. Examples include off-gas hydrogen recovery ( $\text{H}_2/\text{CH}_4$ ), upgrade of carbon monoxide synthesis gas streams ( $\text{H}_2/\text{CO}$ ), helium recovery from natural gas wells ( $\text{He}/\text{N}_2$ ), hydrogen sulfide removal in coal gasification ( $\text{H}_2\text{S}/\text{N}_2$ ), sulfur dioxide removal from combustion gases, carbon dioxide removal in enhanced oil recovery ( $\text{CO}_2/\text{hydrocarbons}$ ), upgrading the heating value of natural gas ( $\text{N}_2/\text{CH}_4$ ), and oxygen enrichment of air ( $\text{O}_2/\text{N}_2$ ).<sup>1–3</sup> Despite these commercially important applications, the selection of polymers to achieve optimum flux and permselectivity for a given separation is still empirical in approach. The factors that contribute to gas permeability are the diffusivity and the solubility of the gas in the polymeric membrane. In the majority of cases, diffusivity (mobility) selectivity is the dominant factor in determining permselectivity.<sup>4</sup> In some cases, such as  $\text{CO}_2/\text{CH}_4$  separation by cellulose acetate<sup>5</sup> and by poly(trifluoropropyl methyl siloxane),<sup>6</sup> solubility selectivity may be controlling due to specific interactions between the gas and certain polymer functional groups. Unfortunately, there has been no direct experimental evidence for such interactions. Pilato et al.<sup>4</sup> suggest that specific interaction (dipole–dipole) between  $\text{CO}_2$  and the sulfone group of polysulfone is the reason for the relatively high solubility selectivity of this polymer. Koros<sup>5,7</sup> has shown that the ratio of  $\text{CO}_2/\text{CH}_4$  Henry's law solubilities ( $k_D$ ) may be quantitatively correlated with the concentration ( $\text{g}/\text{cc}$ ) of sulfone or carbonyl groups for polymers and low molecular weight organics such as ethyl acetate. Representative solubility selectivities are given in Table I.

The present study reports FTIR measurements of cellulose acetate (CA) and poly(methyl methacrylate) (PMMA) under high pressure  $\text{CO}_2$ . The choice

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TABLE I  
 Solubility Selectivity

Medium	$k_D(\text{CO}_2)/k_D(\text{CH}_4)$	Ref.
Poly(2,6-dimethyl-1,4-phenylene oxide)	2.9	5
Polydimethylsiloxane	2.9	b
Polysulfone	4.1	5
Kapton polyimide <sup>a</sup>	4.1	5
Polycarbonate	4.7	5
Poly(trifluoropropyl methyl siloxane)	6.5	b
<b>Poly(methyl methacrylate)<sup>b</sup></b>	<b>9.3</b>	<b>5</b>
Acetone	10.8	5
<b>Cellulose acetate<sup>b</sup></b>	<b>11.4</b>	<b>5</b>
Methyl acetate	11.5	5

<sup>a</sup> Poly[*N,N'*-(phenoxyphenyl) pyromellitimide].

<sup>b</sup> Boldface: V. M. Shah, B. J. Hardy, and S. A. Stern, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 2033 (1986).

of FTIR as a technique to study gas-polymer interactions follows the work of Fowkes and others who have used FTIR to study interactions of polymers with organic liquids,<sup>8,9</sup> inorganic solids such as calcium carbonate and silica,<sup>10,11</sup> and with other polymers.<sup>8,11,12</sup> Fowkes chose to characterize all interactions on the basis of London dispersion and Lewis acid-base (electron acceptor-donor) interactions and has used Drago's classification scheme<sup>13-15</sup> to quantify the donor-acceptor strength of polymers and inorganic surfaces. According to this scheme, "acid gases" like CO<sub>2</sub> and SO<sub>2</sub> are considered to be  $\pi^*$ -electron pair acceptors<sup>16</sup> while polymers like CA and PMMA are electron donors (i.e., Lewis bases).<sup>17</sup> For example, PMMA is known to absorb strongly from solution onto an (acidic) silica surface but not on (basic) calcium carbonate.<sup>18</sup> As shown by data given in Table I, these two polymers exhibit extremely high CO<sub>2</sub> selectivity as would be expected on the above classification.

## EXPERIMENTAL

**Materials.** Poly(methyl methacrylate) was purchased from Polysciences, Inc. Cellulose acetate, 39.8% acetyl content, was purchased from Aldrich Chemical Co. High purity gases were purchased from Union Carbide. These were carbon dioxide, 99.99% purity, and helium, 99.998% purity, and were used without any further treatment.

**Sample Preparation.** Thin films ( $\sim 5 \mu\text{m}$ ) were prepared by casting 1% (g/mL) acetone solutions onto glass. These films were allowed to dry in air and then in vacuum at room temperature for 72 h. They were then placed on the surface of calcium fluoride windows for insertion in the high pressure FTIR gas cell, described below.

**Apparatus.** A high pressure FTIR cell was constructed from 304-SS. A schematic of the cross-sectional view of this accessory is shown in Figure 1. Two optical windows were used at either side of the accessory in modification

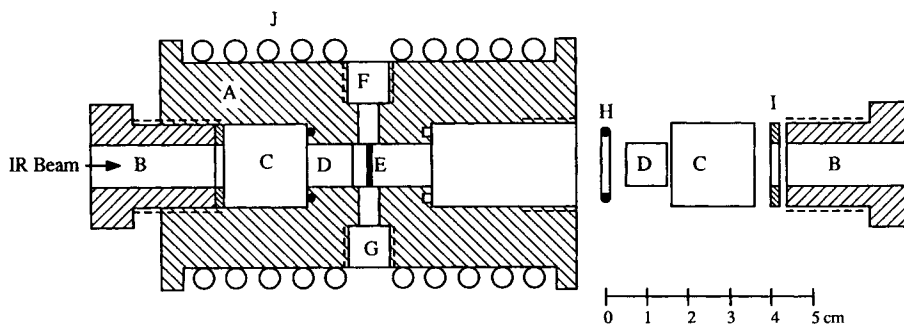


Fig. 1. Schematic diagram of high-pressure FTIR cell: (A) cell body; (B) screw plug; (C) outer window; (D) inner window; (E) cast film; (F) gas inlet port; (G) gas outlet port; (H) Viton O-ring; (I) Teflon gasket; (J) heating coil.

of a step-window design described by Edwards and Schrader.<sup>19</sup> The inner windows (9 mm in diameter and 5 mm in thickness) were fabricated from sodium chloride by Spectra-Tech. Dimensions were 9 mm diameter and 5 mm thickness. These were used to minimize the disturbance of free gas in the light path. The outer window which served to provide the pressure seal was 20 mm in diameter and 20 mm thick. These were either sodium chloride or calcium fluoride obtained from the Harshaw Chemical Co. Sodium chloride and calcium fluoride are visible in the infrared regions, above 600 and 1000  $\text{cm}^{-1}$ , respectively. Sodium chloride has been used at pressures as high as 1000 psi<sup>20</sup> while calcium fluoride has been used at pressures up to 200 atm<sup>21,22</sup> and is the preferred window material for use above 600 psi. A Viton O-ring was used to form the seal between the larger window and cell wall and a Teflon gasket protected the window at its surface against the screw plug used to close the entire assembly.

To maintain constant temperature, the high-pressure cell was wrapped with  $\frac{3}{16}$  in. copper tubing through which water from a constant temperature bath was circulated. For these experiments, a temperature of 35°C was used because it is the temperature most frequently used to report dual-mode parameters. The entire assembly sits in the FTIR sample chamber as shown in Figure 2. The cell may be evacuated by means of a vacuum pump or pressurized with He or CO<sub>2</sub> from a commercial gas cylinder.

**Measurements.** Each film sample was conditioned at  $35 \pm 1^\circ\text{C}$  in the high pressure cell at the measurement pressure for a period of 1.5 h which was considered adequate to achieve sorption equilibrium of the thin films used in this study. Infrared spectra of the conditioned films were obtained by use of a Digilab FTS-60 Fourier transform infrared (FTIR) spectrophotometer equipped with a DTGS detector and operating at a resolution of 2  $\text{cm}^{-1}$ . A minimum of 150 scans was signal-averaged.

## RESULTS AND DISCUSSION

Sorption isotherms of glassy polymers follow the dual-mode model,<sup>23</sup> where the concentration of sorbed-gas is given as

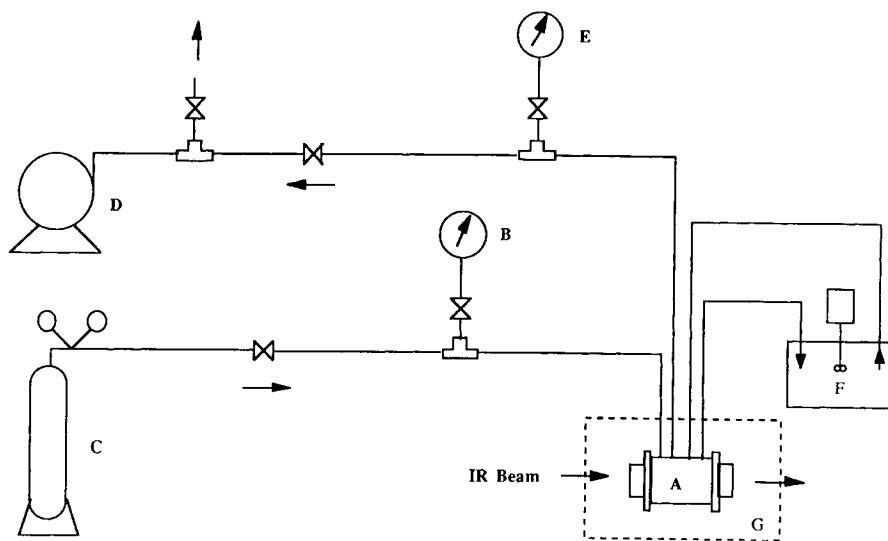


Fig. 2. Experimental setup for high-pressure FTIR measurements: (A) high-pressure FTIR cell (Fig. 1); (B) vacuum gauge; (C) gas cylinder; (D) vacuum pump; (E) pressure gauge; (F) temperature controller; (G) FTIR sample chamber.

$$C = C_D + C_H = k_D p + C'_H b p / (1 + b p) \quad (1)$$

where  $C_D$  represents the concentration of sorbed gas in the (Henry's law) dissolution mode and  $C_H$  represents the concentration in the Langmuir sites, non-equilibrium packets of free volume or microdomains of lower density. The parameters in eq. (1) are  $k_D$ , Henry's law constant;  $p$ , pressure;  $C'_H$ , the Langmuir capacity term; and  $b$ , the (Langmuir) hole affinity parameter. Solubility data for  $\text{CO}_2$  in PMMA and in CA at high pressures have been widely published. The maximum  $\text{CO}_2$  pressure used in the FTIR measurements was 55 atm (800 psig). This represents a subcritical state for  $\text{CO}_2$  for which the critical temperature is  $31.1^\circ\text{C}$  and the critical pressure is 72.8 atm; the vapor pressure of  $\text{CO}_2$  at  $21^\circ\text{C}$  is 820 psig or 56.5 atm. At  $35^\circ\text{C}$  and the maximum measurement pressure of 55.5 atm, solubility of  $\text{CO}_2$  is estimated from dual-mode parameters of PMMA<sup>24</sup> to be 52.4 cc  $\text{CO}_2$  (STP)/ $\text{cm}^3$  PMMA (8.6 wt %) and from dual-mode parameters for CA<sup>25</sup> to be 41.4 cc  $\text{CO}_2$  (STP)/ $\text{cm}^3$  CA (6.3 wt %).

FTIR measurements for  $\text{CO}_2$ -conditioned CA indicate a small but distinct frequency shift of the carbonyl stretching vibration at  $1752\text{ cm}^{-1}$  to higher wavenumbers as shown in Figure 3 by comparison of spectra peaks for a samples conditioned in vacuum and at the maximum pressure of 55 atm  $\text{CO}_2$ . This shift increases with increasing  $\text{CO}_2$  pressure as shown by the difference spectra in Figure 4. Also, as indicated by the difference spectra, there is only a small shift for samples conditioned at 55 atm helium pressure. Since helium is only slightly soluble in CA, the observed frequency shifts in the CA/ $\text{CO}_2$  system cannot be due to pressure effects alone but must result from the interaction of sorbed  $\text{CO}_2$  with the carbonyl group of CA.

Figure 5 shows the observed shift in the carbonyl stretching frequency of PMMA ( $1731\text{ cm}^{-1}$ ) at 55-atm  $\text{CO}_2$ . This shift is comparable to that observed

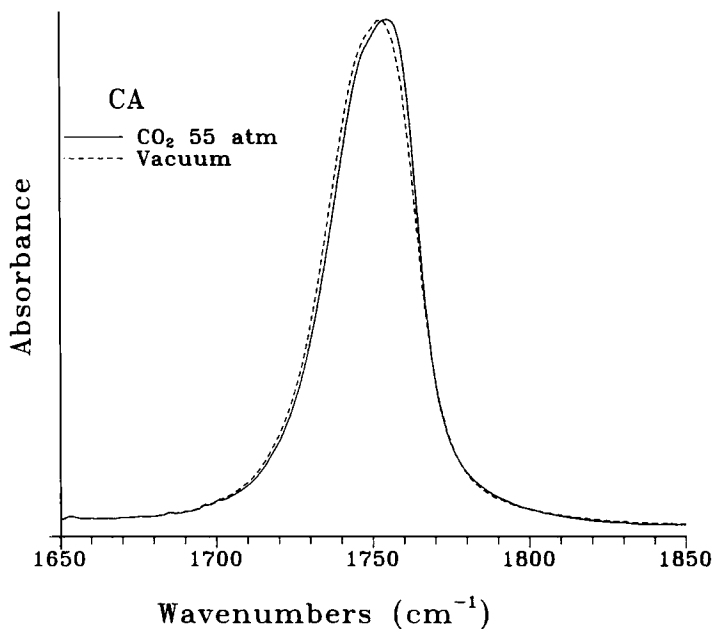


Fig. 3. Comparison of carbonyl stretching vibrations of cellulose acetate at 0 (---) and 55 (—) atm  $\text{CO}_2$  pressure.

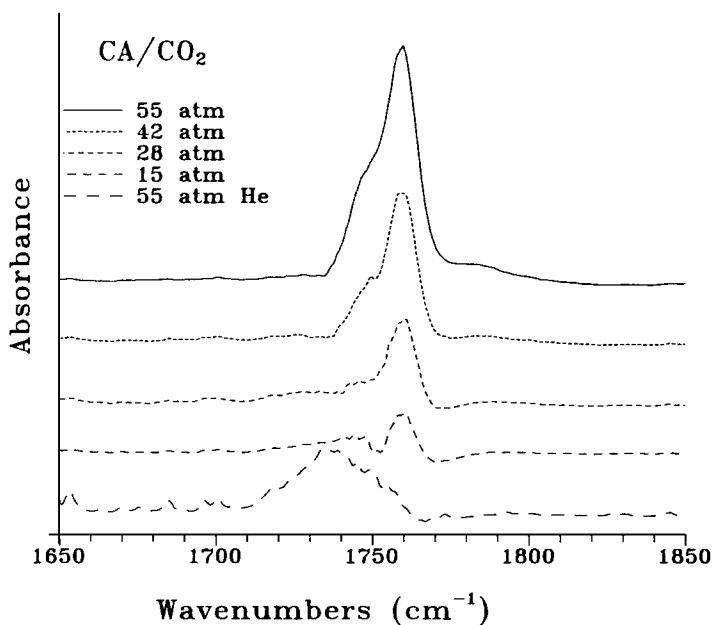


Fig. 4. Difference spectra for carbonyl stretching vibrations of cellulose acetate samples conditioned at 15, 28, 42, and 55 atm  $\text{CO}_2$  pressure and a sample conditioned in vacuum. For comparison the difference spectra for a sample conditioned at 55-atm He pressure is shown (bottom curve).

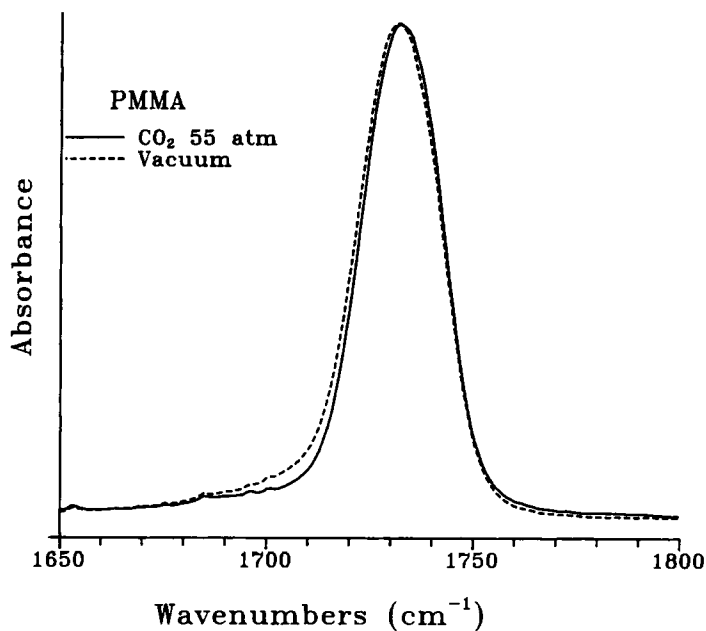


Fig. 5. Comparison of carbonyl stretching of poly(methyl methacrylate) at 0 (---) and 55 atm (—) CO<sub>2</sub> pressure.

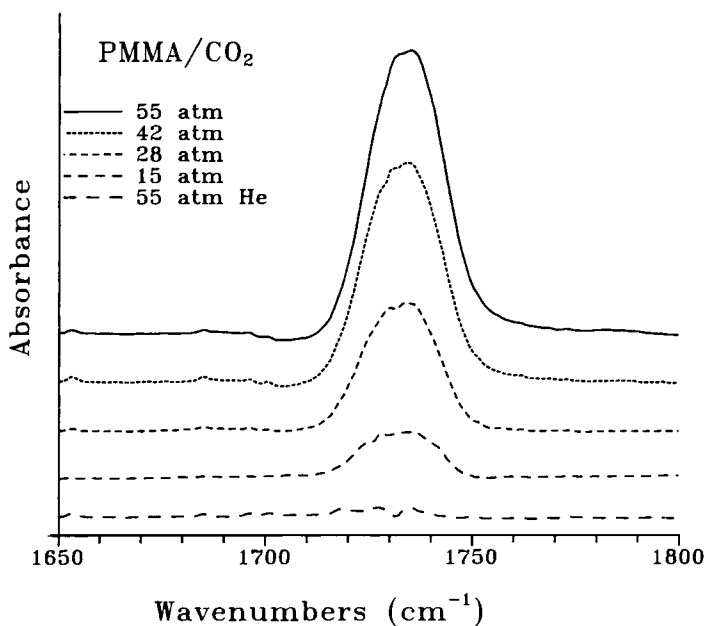


Fig. 6. Difference spectra for carbonyl stretching vibrations of PMMA samples conditioned at 15, 28, 42, and 55 atm CO<sub>2</sub> pressure and a sample conditioned in vacuum. For comparison, the difference spectrum for a sample conditioned at 55-atm He pressure is shown (bottom curve).

for CA. The effect of pressure on this shift is shown by the difference spectra in Figure 6. In the case of helium, virtually no shift is observed at 55 atm pressure compared to the small shift observed for CA/He.

The observed shifts in the carbonyl stretching frequencies of CA and PMMA (ca.  $2\text{ cm}^{-1}$  at 55 atm  $\text{CO}_2$ ) are significantly smaller than the  $10\text{--}30\text{ cm}^{-1}$  shifts typically observed in the case of strong dispersive<sup>8</sup> or Lewis acid-base<sup>26</sup> interactions and may be associated with weak dipole-dipole interactions between  $\text{CO}_2$  and the carbonyl group. Since the dual-mode model<sup>23</sup> postulates the existence of two different environments for sorbed gas, i.e., the Henry's law dissolution and Langmuir modes, it is useful to correlate the pressure dependence of the shifts with gas concentration as represented by the dual-mode equation [eq. (1)]. Since the Langmuir sites are believed to be regions of localized excess volume (microvoids), it is reasonable to suggest that gas-polymer interactions may occur only in the dissolution mode where  $C_D = k_D p$ . Furthermore, the absorbance of the  $\text{CO}_2$ -interactive groups therefore should be proportional to  $C_D$  from the statement of Beer's law. Figures 7 and 8 show the relative absorbances of the difference spectra for CA and PMMA, respectively, vs.  $k_D p$ , where  $k_D$  values have been taken from the literature as cited earlier ( $0.944\text{ cm}^3\text{ (STP)}/\text{cm}^3\text{ atm}$  for PMMA<sup>24</sup> and  $k_D = 0.7455\text{ cm}^3\text{ (STP)}/\text{cm}^3\text{ atm}$  for CA<sup>25</sup>). For both CA and PMMA, the resultant plots appear linear within experimental error.

## CONCLUSIONS

In the case of two carbonyl-containing polymers showing high  $\text{CO}_2$  solubility, gas-polymer interactions appear to be weak dipole-dipole interactions occurring

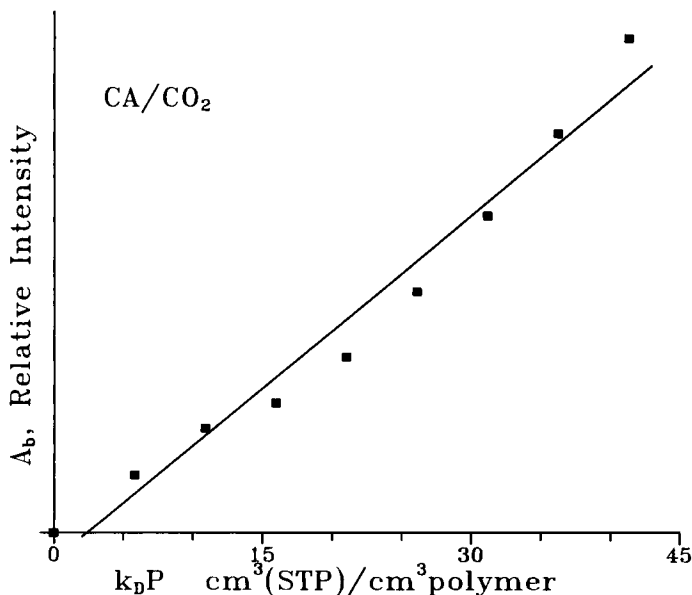


Fig. 7. Plot of the absorbance intensities (peak height) of difference spectra ( $A_b$ ), arbitrary units, vs. the product of Henry's law constant ( $k_D$ ) and pressure ( $p$ ) for CA. The line represents least squares fit of data.

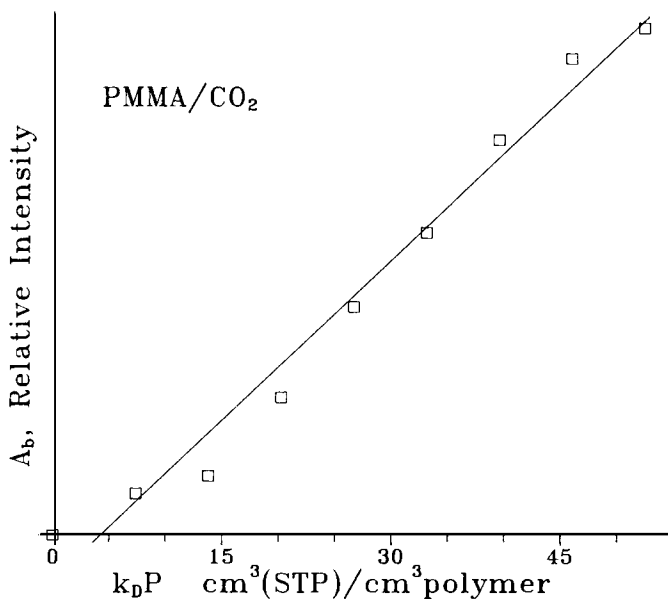


Fig. 8. Plot of the absorbance intensities (peak height) of difference spectra ( $A_b$ ), arbitrary units, vs. the product of Henry's law constant ( $k_D$ ) and pressure ( $p$ ) for PMMA. The line represents least squares fit of data.

between the carbonyl group and  $\text{CO}_2$ . The dependence of carbonyl frequency shift on  $\text{CO}_2$  pressure appears to follow a Henry's law relationship for  $\text{CO}_2$  concentration. This suggests that gas sorbed in the Langmuir sites of glassy polymers may not participate in specific interaction with the polymer.

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