

Hydrophobic films for optical detection of dry carbon dioxide based on ion pairing and an amine polymer

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Abstract—Existing optical carbon dioxide sensors using ion pair materials with pH indicators need moisture to function. To sense dry carbon dioxide gas, hydrophobic films were prepared using an amine polymer (branched-polyethyleneimine) instead of water, along with an ion pair dye and an aromatic polymer. The color of the ion pair formed between cresol red sodium salt and tetra-n-octylammonium bromide was yellow when the pH was below neutral. After adding branched polyethyleneimine, the color changed to violet as the pH became basic. On exposure to carbon dioxide, the amine groups on the branched-polyethyleneimine were converted to alkyl carbamate anions and ammonium cations via reaction with the carbon dioxide. When the ion pair reacted with the resulting ammonium cations, the film changed color from violet to yellow. It was determined that the degree of color change was dependent on the carbon dioxide exposure times and the amount of branched-polyethyleneimine added to the film.

Keywords: Cresol Red, Ion Pair Dye, Dry Carbon Dioxide Sensor, Amine Polymer, Hydrophobic Sensor

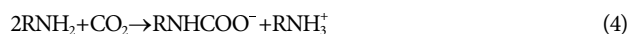
INTRODUCTION

Carbon dioxide measurement techniques are used in various fields, including chemical, clinical breath, and environmental monitoring [1]. There are two major classes of optical carbon dioxide sensor. The first is based on a carbon dioxide-induced change in the fluorescence of luminescent dyes such as 1-hydroxypyrene-3, 6, 8-trisulfonate or ruthenium(II) complexes [2-5]. The second type is based on a colorimetric change of a pH indicator dye such as thymolsulfonphthalein (thymol blue), phenolsulfonphthalein (phenol red), or cresol red [6-8]. The Wolfbeis group [9-12] studied a quaternary ammonium cation (Q^+) and pH indicator dye anion (D^-) system as a dye-based optical sensor. Their studies showed that the reaction between the Q^+D^- ion pair and carbon dioxide requires water for a color change to occur. The color change reaction of the Q^+D^- ion pair dye is shown in Eqs. (1)-(3).



The dye molecules (DH) and the quaternary cations (Q^+OH^-) form hydrated ion pairs (Q^+D^-), where Q^+ represents the positively charged quaternary ammonium cation. The ion pair reacts with carbon dioxide to give a new ion pair composed of Q^+ and HCO_3^- , thereby protonating the indicator dye and changing its absorption maximum.

We studied an ion-pair indicating material using an amine group and bPEI to detect non-polar carbon dioxide gas without the influence of water molecules. When the amine groups absorb carbon dioxide [13], the change in the pH causes the alkali amines to form a carbamate anion and an ammonium cation [14], as shown in Eqs. (4) and (5).



At neutral pH, the alkyl amine changed to an alkyl carbamic acid formed from an alkyl carbamate anion and an alkyl ammonium cation [15-19]. Cresol red sodium salt and tetrabutyl ammonium bromide were also used to form a hydrophobic ion pair dye as a pH indicator dye contained within polystyrene with a high gas permeability [20], which was used to form a hydrophobic film.

The reaction mechanisms and optical characterizations of hydrophobic films for optical sensing of dry carbon dioxide according to the amount of amine added are described in this paper.

MATERIALS AND METHODS

1. Materials

Cresol red sodium salt (Na^+CR^-) and tetra-n-octylammonium bromide (TOA^+Br^-) were purchased from Tokyo Chemical Industry Co. Ltd. and Acros Organics, Japan, respectively. Polystyrene (PS, Mw=280,000) and branched polyethyleneimine (bPEI, Mw=25,000) were from Sigma Aldrich, Korea. Methanol (99.5%), toluene (99.8%) (Samchun Chemicals Co. Ltd., Korea), chloroform (99.8%, Sigma Aldrich, Korea), and deionized water were used as solvents. Deuteriochloroform ($CDCl_3$, 99.8 atom% D, contains 0.03% TMS) was

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purchased from Aldrich for ^1H -nuclear magnetic resonance (NMR) spectroscopy.

2. Preparation of TOA^+CR^- Ion Pair Dye

To prepare printable polyolefin films containing a hydrophobic carbon dioxide sensing dye, it was necessary for the hydrophilic Na^+CR^- dye to be converted to a hydrophobic ion pair dye. Methanol (40 v/v%) and toluene (60 v/v%) were used as co-solvents. Na^+CR^- (500 mg, 1.23 mmol) was dissolved in 100 ml of the co-solvents. In a separate flask, TOA^+Br^- (675 mg, 1.23 mmol) was dissolved in 50 ml of the co-solvents. The TOA^+CR^- ion pair was formed by dropwise addition of the Na^+CR^- solution to the TOA^+Br^- solution. Then, 150 ml of deionized water was poured into the TOA^+CR^- ion pair solution. This allowed the toluene and methanol to be separated using the liquid-liquid extraction method. The methanol/aqueous solution was removed, and the methanol/toluene solution was washed twice more with deionized water. The residual toluene solution was then dried in a vacuum oven overnight to yield the TOA^+CR^- ion pair dye.

3. Preparation of Carbon Dioxide Sensitive TOA^+CR^- Ion Pair Film

For the solution casting method, a 10 wt% solution of PS in chloroform was prepared in one flask, while a 10 wt% solution of bPEI in chloroform was prepared in a separate flask. The six sample solutions were each prepared by first dissolving 9 mg of the TOA^+CR^- ion pair dye in 6.67 ml of the PS solution to give a yellow color. After this, 0, 20, 40, 60, 80, and 100 μl of the bPEI solution were added to each sample solution, resulting in the solutions containing bPEI changing color to violet. Next, 1 ml of each sample solution was dropped onto separate polytetrafluoroethylene (PTFE) sheets and cast to a thickness of $22 \pm 1 \mu\text{m}$ using the doctor blade method. The resulting films were dried for 15 min under atmospheric conditions.

4. Characterization of TOA^+CR^- Ion Pair Dye and Carbon Dioxide Sensitive Films

^1H NMR analysis of TOA^+CR^- with and without bPEI was performed in CDCl_3 solutions in Wilmad® quick pressure valve 5 mm diameter NMR tubes before and after exposure to inert carbon dioxide gas. Spectra were measured using a Bruker-Spectrospin 300 MHz spectrometer at 25°C , with chemical shifts (δ) expressed in parts per million (ppm) by frequency, using tetramethylsilane (TMS, $\delta\text{H}=0$) as an internal standard.

Indicator films were measured by UV-vis spectrometer (UVIKON XS) between 350 and 800 nm after set carbon dioxide purge times to confirm changes in visible light absorption. Carbon dioxide gas (99.999%) was used, and purging velocity was 50 ml/min as determined by a flow controller (Shimadzu, FC-60A).

To show the color changes in the carbon dioxide sensitive films, pictures and video (as shown in the supplementary information) were taken with a digital camera (Nikon D800, AF-S Micro NIKKOR 60 mm, f/2.8G ED) before and after purging with carbon dioxide. The white balance and scene mode were automatic. The sensitivity of the indicator films according to carbon dioxide purging time was measured using CIELab color space and a spectrophotometer (X-Rite Co. Ltd., SpectroEye). In the CIELab system, L^* represents the lightness, a^* represents the degree between red (positive value) and green (negative value), and b^* represents the

degree between yellow (positive value) and blue (negative value) in the color space [21]. The color difference (ΔE^*) indicates the distance between two samples in the color space, as shown in Eq. (6).

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5} \quad (6)$$

ΔE^* was calculated from the distance between the film before contact with carbon dioxide and the film after contact with carbon dioxide.

RESULTS AND DISCUSSION

1. Transition from Amine to Ammonium Cation in TOA^+CR^- CDCl_3 Solution with bPEI

^1H NMR spectra of TOA^+CR^- were measured with and without bPEI, and before and after exposure to carbon dioxide, as shown in Fig. 1. All spectra exhibited the methylene ($\alpha=3.2$ ppm, $\beta=1.3$ ppm) and methyl protons ($\beta=0.96$ ppm) of the TOA^+ chain [22], as well as the benzene (7.1–7.3 ppm), ethylene (6.5, 7.2, and 7.3 ppm), and methyl protons (2.0 and 2.4 ppm) of CR^- [23]. The spectra of TOA^+CR^- with bPEI showed the amine protons of bPEI (2.0 ppm) [24,25]. After bubbling with carbon dioxide, the spectrum of TOA^+CR^- with bPEI showed an ammonium cation peak (7.3 ppm) that was more intense than that seen in other samples. Thus, it was determined that many ammonium cations were formed after bubbling carbon dioxide through the TOA^+CR^- solution containing bPEI.

The color of the TOA^+CR^- CDCl_3 solution for NMR analysis was yellow. As shown on the left in Fig. 2, the cresol red molecule maintained its dye (DH) form and an ionic bond with the TOA^+ cation (Q^+). When the bPEI was added to the TOA^+CR^- solution, the color changed to violet. CR-H transformed to the CR^- anion (shown in Eq. (7) and on the right in Fig. 2) as the proton was transferred to the bPEI amine (bold proton on the left of Fig. 2), converting this amine to an ammonium cation and changing the color

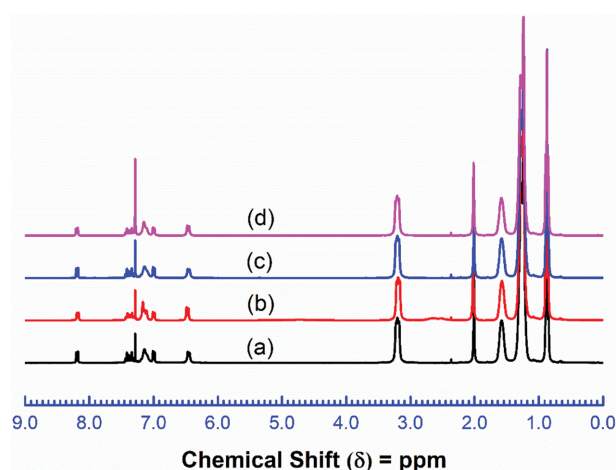


Fig. 1. ^1H -NMR spectra of TOA^+CR^- CDCl_3 solutions with and without bPEI before and after exposure to inert carbon dioxide gas. (a) TOA^+CR^- , (b) TOA^+CR^- with bPEI, (c) TOA^+CR^- after exposure to inert carbon dioxide, and (d) TOA^+CR^- with bPEI after exposure to inert carbon dioxide.

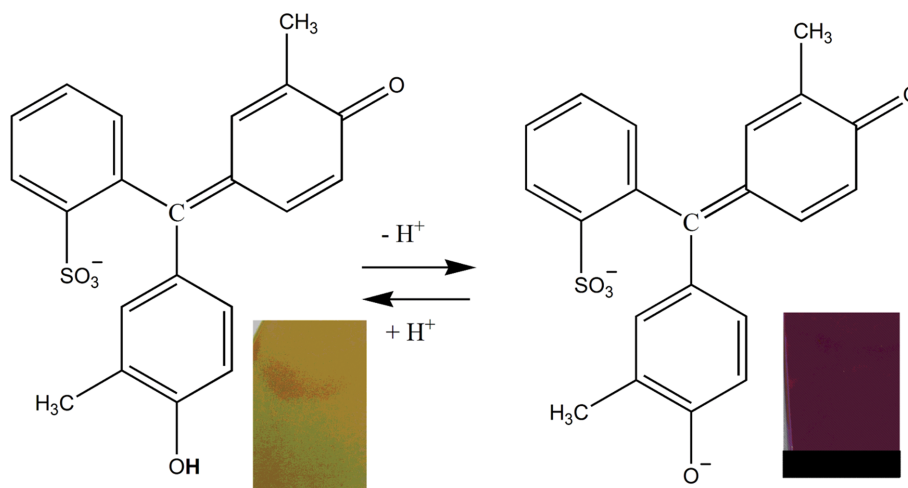


Fig. 2. The acidic and basic forms of cresol red. The color of cresol red is yellow below pH 7.2 and violet above pH 8.8. The labile proton of the dye is shown in bold: removal of this proton causes the acidic form of dye to convert to the basic form of dye.

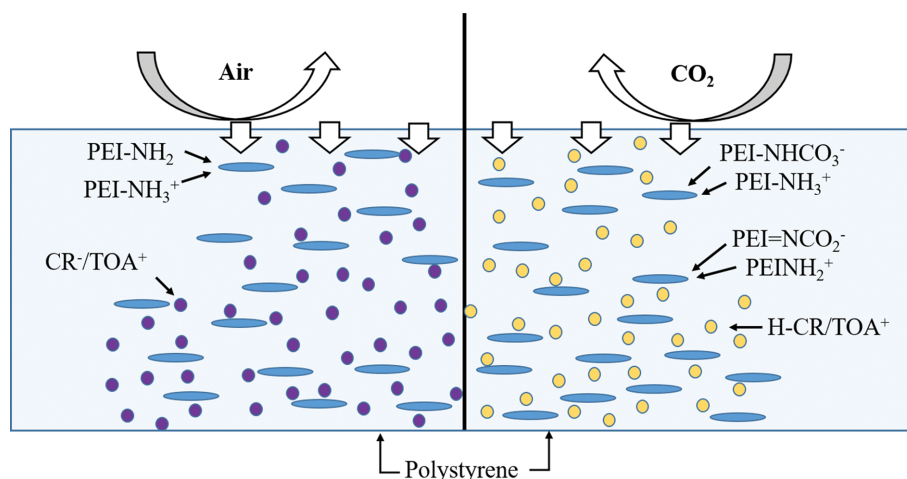
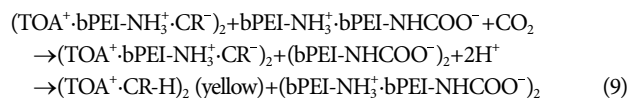
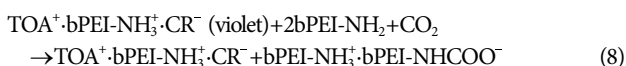
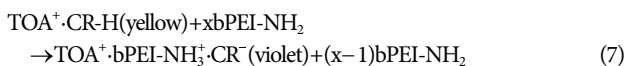


Fig. 3. Cross-section of a sensor film and a schematic representation explaining the effect of changing the dye by reaction with amine and carbon dioxide.

of the solution to violet. When carbon dioxide was injected into the TOA⁺CR⁻ solution containing bPEI, the polymer reacted with the carbon dioxide to form an alkyl carbamate anion and an alkyl ammonium cation. The alkyl ammonium cation was then converted to another alkyl carbamate anion through further reaction with carbon dioxide, generating protons [18]. The color of the TOA⁺CR⁻ solution containing bPEI changed from violet back to yellow after injection of carbon dioxide due to the reaction between these generated protons and the CR⁻ anion [26], which led to CR-H being reformed (shown in Eqs. (7)-(9)). The TOA⁺ cation was unchanged as it acted as a phase transfer agent. The color of the TOA⁺CR⁻ CDCl₃ solution changes reversibly depending on the external stimuli (acid or base conditions).



The use of the hydrophobic films as optical sensors for dry carbon dioxide was investigated. These films consisted of solutions of TOA⁺CR⁻ and bPEI in PS. PS was chosen because it is impermeable to protons but highly permeable to carbon dioxide [20]. The PS solutions were spread onto PTFE to form films with thicknesses of 22±1 μm after solvent evaporation. A cross-sectional scheme of a sensor film is shown in Fig. 3. When carbon dioxide penetrates the PS film, it reacts with the bPEI amine to form an alkyl carbamate anion and an alkyl ammonium cation. Once additional carbon dioxide has penetrated the film, protons are generated from the reaction between the alkyl ammonium cations and carbon dioxide to form alkyl carbamate anions, after which the CR⁻ anions react with the protons and form CR-H. The pK_a of this reaction is known to be 8.15 [23].

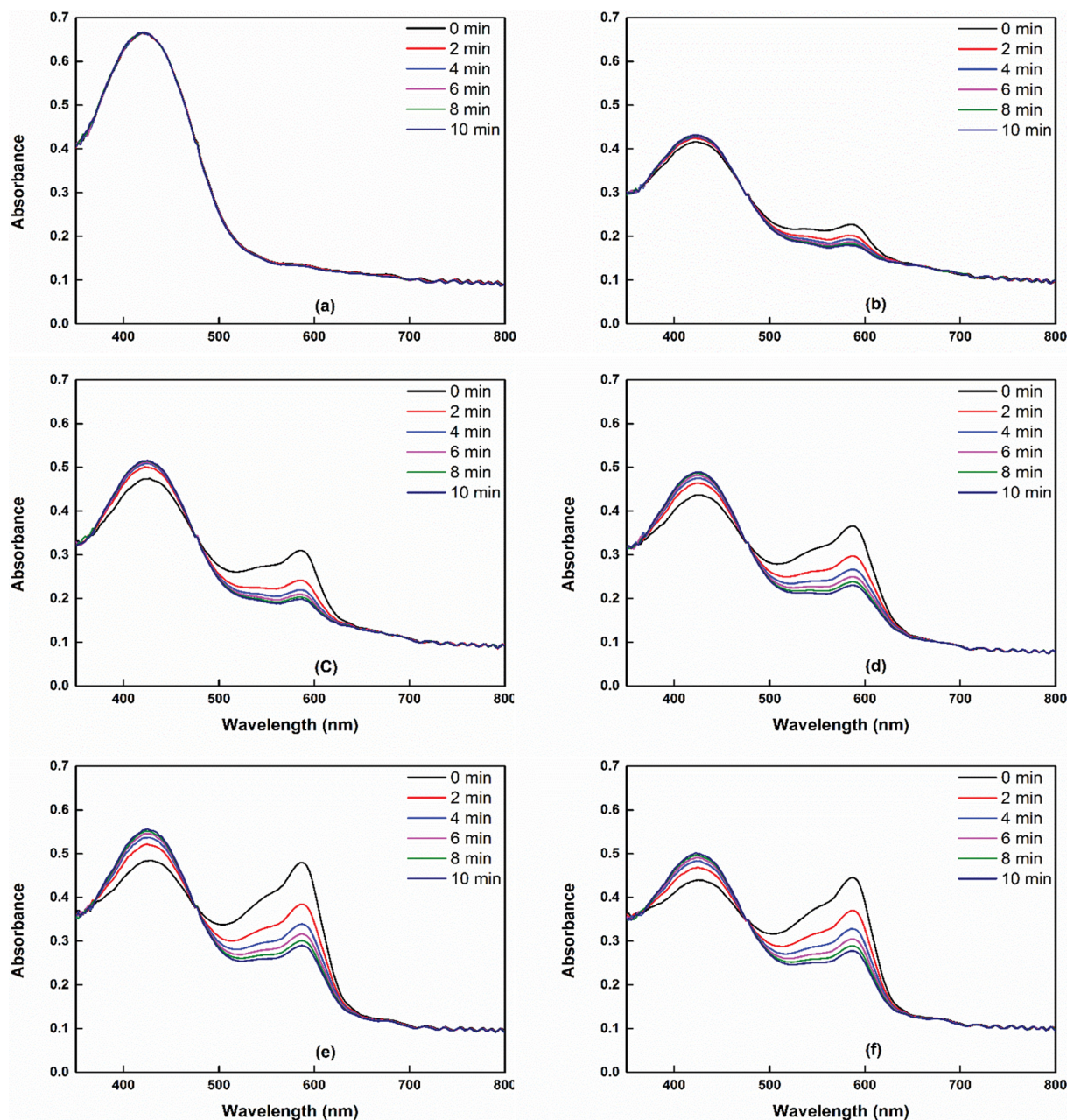


Fig. 4. Absorption spectra of TOA⁺CR⁻ ion pair films with and without bPEI after different lengths of exposure to carbon dioxide (0, 2, 4, 6, 8, and 10 minutes). (a) TOA⁺CR⁻ ion pair film, (b) TOA⁺CR⁻ ion pair film with 20 μ l bPEI, (c) TOA⁺CR⁻ ion pair film with 40 μ l bPEI, (d) TOA⁺CR⁻ ion pair film with 60 μ l bPEI, (e) TOA⁺CR⁻ ion pair film with 80 μ l bPEI, and (f) TOA⁺CR⁻ ion pair film with 100 μ l bPEI.

2. Changes in Absorption Spectra of Films with Carbon Dioxide Exposure Times

As shown in Fig. 4, films containing only the TOA⁺CR⁻ ion pair showed no changes in absorption spectra before and after carbon dioxide exposure. When bPEI was added to TOA⁺CR⁻ ion pair films, the light absorption decreased at 420 nm and dramatically increased at 590 nm, changing the color of the film from yellow to violet. When these films were exposed to carbon dioxide, absorption at 420 nm increased while absorption at 590 nm dramatically decreased with increasing carbon dioxide exposure times. Thus,

when TOA⁺CR⁻ ion pair films with bPEI were exposed to carbon dioxide, the color changed from violet back to yellow. The thickness of these films was slightly different; therefore, comparisons of absolute changes in the absorptions of these films were difficult. By comparing the relative absorptions of the films, it can be seen that as the amount of bPEI added was increased, the degree of absorbance change at 420 nm slightly decreased, while the change at 590 nm dramatically increased. This is because ammonium cations were formed via the reaction between amine and carbon dioxide, and these ammonium cation and the CR⁻ anions formed bonds.

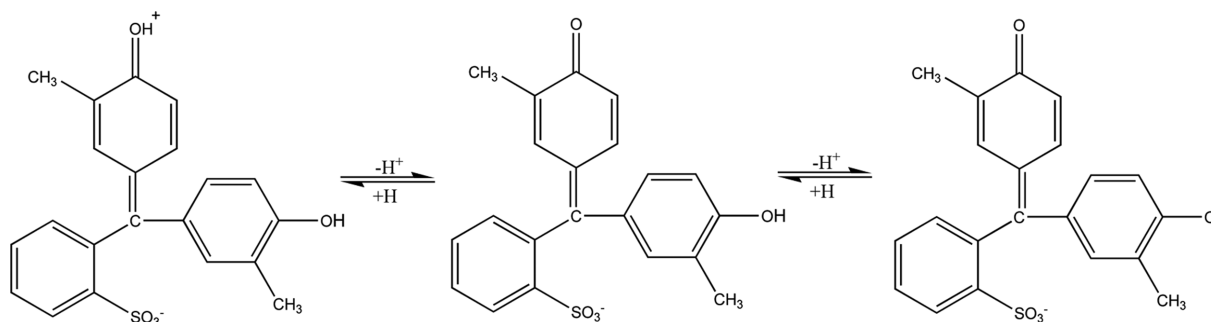


Fig. 5. The change from CR-H to the CR-H₂⁺ cation in the presence of excess protons. The color and maximum absorption wavelength of CR-H₂⁺ in the region of interest are orange-red and 518 nm, respectively.

However, the TOA⁺CR⁻ ion pair film containing 100 μ l of bPEI showed a smaller decrease at 420 nm and a smaller increase at 590 nm than the film containing 80 μ l of bPEI. This was considered to be because the amounts of alkyl carbamate anions, alkyl ammonium cations, and protons formed affected the color of the film. According to Henger et al. [23], the yellow CR-H transforms to the orange-red CR-H₂⁺ cation on addition of a second proton. This reaction scheme is shown in Fig. 5, and the pK_a of this reaction is known to be 1.11 [23]. As CR-H₂⁺ absorbs at 518 nm, the conversion of CR-H to CR-H₂⁺ in the presence of 100 μ l of bPEI resulted in the reduced absorption intensity at 590 nm.

At high levels of bPEI, the change in light absorption would be expected to be slow due to the nature of the conversion of amines to ammonium cations via pH change to react with carbon dioxide. However, as the amount of bPEI added was increased, the amount of ammonium cations formed increased, thus generating more protons and carbamates due to the reaction between ammonium cations and carbon dioxide, and therefore the amount of CR- converted to CR-H increased. Thus, on contact with carbon

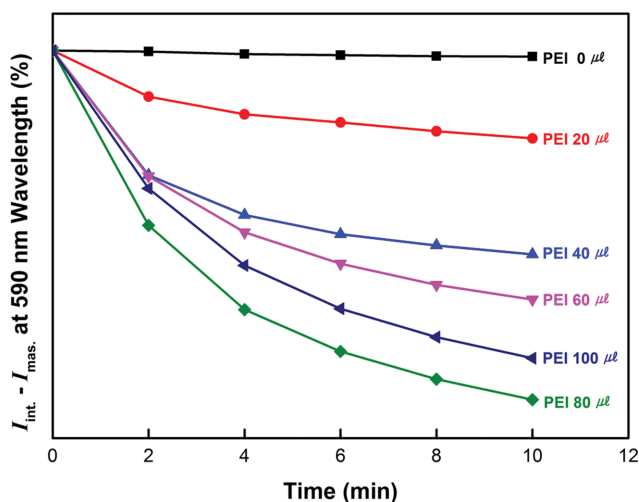


Fig. 6. The intensity difference ($I_{\text{int}} - I_{\text{mas}}$) between the initial TOA⁺CR⁻ ion pair films and those exposed to carbon dioxide at 590 nm. This was compared for each film.

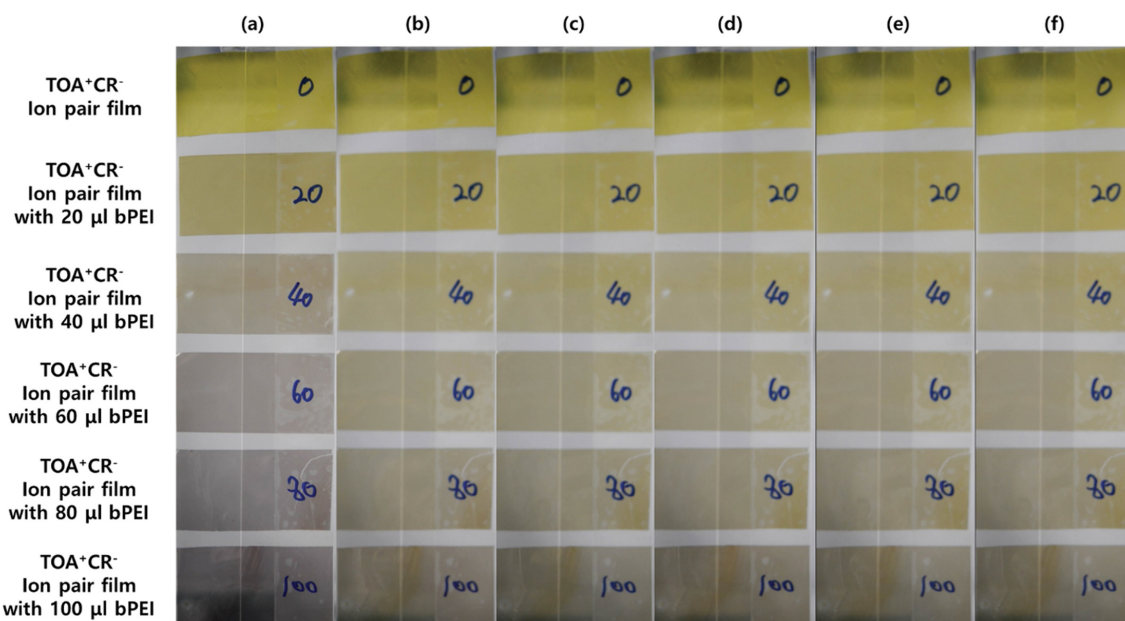


Fig. 7. Images of TOA⁺CR⁻ ion pair films with and without bPEI according to carbon dioxide exposure time. (a) Initial time, (b) after 2 min, (c) 4 min, (d) 6 min, (e) 8 min, and (f) 10 minutes.

Table 1. The values of ΔE^* , L^* , a^* , and b^* for TOA⁺CR[−] ion pair dye films with various amounts of bPEI after different carbon dioxide contact times ($\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5}$)

Additional bPEI sol. ^a	Value ^b	0 (min)	2 (min)	4 (min)	6 (min)	8 (min)	10 (min)
0 μl	L^*	85.93	85.92	85.92	85.92	85.89	85.98
	a^*	−9.55	−9.56	−9.56	−9.56	−9.56	−9.59
	b^*	58.64	58.6	58.55	58.56	58.53	58.56
	ΔE^*	0	0	0.091104	0.08124	0.117473	0.10247
20 μl	L^*	83.48	84.22	84.46	84.56	84.65	84.73
	a^*	−5.46	−6.03	−6.1	−6.13	−6.17	−6.2
	b^*	24.35	26.76	27	27.19	27.36	27.53
	ΔE^*	0	2.584686	2.896981	3.111414	3.306524	3.496069
40 μl	L^*	78.82	80.29	80.66	80.86	81.02	81.06
	a^*	−4.73	−5.6	−5.77	−5.86	−5.92	−5.99
	b^*	31.72	34.42	35.1	35.47	35.77	35.99
	ΔE^*	0	3.194965	3.986427	4.415994	4.760105	4.983784
60 μl	L^*	78.7	80.97	81.42	81.54	81.81	81.97
	a^*	−3.69	−4.99	−5.24	−5.37	−5.5	−5.59
	b^*	27.87	32.42	33.27	33.7	34.04	34.36
	ΔE^*	0	5.248371	6.241867	6.699022	7.142626	7.511524
80 μl	L^*	72.58	76.69	77.49	77.93	78.21	78.44
	a^*	−1.13	−3.62	−4.08	−4.32	−4.49	−4.62
	b^*	28.51	36.84	38.55	39.24	39.79	40.23
	ΔE^*	0	9.616709	11.55907	12.40691	13.04703	13.56017
100 μl	L^*	77.65	80.27	80.77	80.96	81.16	81.23
	a^*	−2.94	−4.66	−4.95	−5.08	−5.19	−5.28
	b^*	24.45	29.67	30.65	31.05	31.41	31.74
	ΔE^*	0	6.088612	7.22596	7.687373	8.113211	8.451988

^aThe volume of additional 10 wt% bPEI in chloroform solution used to prepare the film samples, which contained 10 wt% PS and 9 mg of the TOA⁺CR[−] ion pair dye

^bCalculated ΔE^* and measured values using the CIELab color space

dioxide, the change in absorption intensity at 590 nm sequentially increased as both the amount of bPEI and the carbon dioxide contact time increased, as shown in Fig. 6. The intensity of the indicator without bPEI does not change with time, but the intensity change was larger with time as the amount of bPEI applied increased to 20, 40, 60, and 80 μl . However, the absorption of indicator with 100 μl of bPEI decreased slightly. This is due to the conversion of CR-H to CR-H₂⁺ as described in Fig. 5.

3. Color Changes According to Carbon Dioxide Exposure times

TOA⁺CR[−] ion pair films with and without bPEI were observed according to carbon dioxide exposure time, as shown in Fig. 7. The TOA⁺CR[−] ion pair film without bPEI was a bright yellow color and did not change at all regardless of exposure time. The TOA⁺CR[−] ion pair films with 20 and 40 μl of bPEI changed to light yellow from yellowish-light purple and light purple, respectively, after 2 min of exposure to carbon dioxide. The TOA⁺CR[−] ion pair films with 60 and 100 μl of bPEI changed from purple and dark purple to yellow and dark yellowish-purple after 4 min. The TOA⁺CR[−] ion pair film with 80 μl of bPEI changed from violet to yellowish-light purple after 2 min and to yellow after 6 min.

Determining the positions of samples in the CIELab color space

allows complex indication of colors and brightness in the visible light range, in contrast with UV-visible absorption spectra. As shown

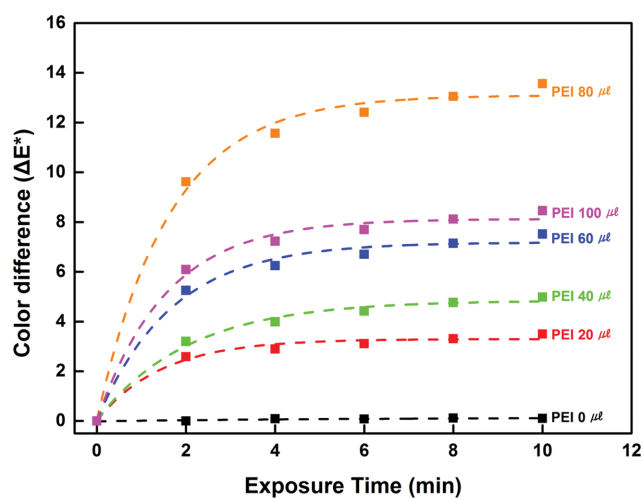


Fig. 8. ΔE^* according to carbon dioxide exposure time as calculated from L^* , a^* , and b^* in the CIELab color space.

in Table 1 and Fig. 8, the brightness (L^*) and color (a^* and b^*) of the TOA⁺CR⁻ ion pair film without bPEI did not change, and ΔE^* showed very little variation. The brightness and color of the TOA⁺CR⁻ ion pair dye film with 20 μ l of bPEI shifted from red and blue colors to bright green (negative shift) and yellow (positive shift), respectively. The ΔE^* of the TOA⁺CR⁻ ion pair film with 20 μ l bPEI showed a curve that reached saturation after 2 min. The films containing 40 and 60 μ l of bPEI showed similar phenomena, although with greater degrees of change. The ΔE^* curves of these films reached saturation after 2 and 4 min, respectively. The film containing 80 μ l of bPEI dramatically shifted to yellow (positive shift) and green (negative shift). The ΔE^* curve of this film showed a continual increase. The film containing 100 μ l of bPEI was less shifted than that containing 80 μ l of bPEI, which showed the largest shift from a blue color to yellow in the 2 minutes after initial contact with carbon dioxide. As the amount of bPEI solution added increased, the amount of protons generated from amines increased and the violet CR⁻ was converted to the yellow CR-H. The reduced change in the CIELab color space values when using 100 μ l of bPEI solution was considered to be due to the formation of the CR-H₂⁺ cation [23].

CONCLUSIONS

The existing method for optical carbon dioxide sensing using a pH indicator dye and a phase transfer agent ion pair requires moisture to function. This study utilized an amine polymer that does not need moisture to achieve the same goal. The amine polymer, branched polyethyleneimine, absorbed carbon dioxide and the amine groups were converted to protons and carbamate anions via ammonium cations and carbamate anions. The results of this study show that a hydrophobic optical ion pair dye could be used to sense carbon dioxide. We also identified the mechanism of dry carbon dioxide detection when using a TOA⁺CR⁻ ion pair dye and the amines of bPEI as a sensor. As the amount of bPEI added was increased, the color change of the ion pair dye was dramatically altered. However, using an excess of amine with the ion pair dye resulted in a reduced color change due to the formation of the orange-red D⁻H₂⁺ cation. The optimal amount of amine seems to depend on the amount of ion pair dye used. Therefore, an ion pair dye and amine system can be used to detect carbon dioxide concentration or exposure time by controlling the amount of ion pair dye and amine used. This ion pair dye and amine polymer system could be printed on polyester and composited with several polymers using this mechanism. Therefore, this system could be used for a variety of applications in the packaging industry, safety appliances, and environmental analysis.

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REFERENCES

1. N. Nakamura and Y. Amao, *Anal. Bioanal. Chem.*, **376**, 642 (2003).
2. M. D. Marazuela, M. C. M. Bondi and G. Orellana, *Sensor. Actuat. B Chem.*, **29**, 126 (1995).
3. O. S. Wolfbeis and L. J. Weis, *Anal. Chem.*, **60**, 2028 (1988).
4. A. Mills and Q. Chang, *Analyst*, **118**, 839 (1993).
5. C. von Bültzingslöwen, A. K. McEvoy, C. McDonagh and B. D. MacCraith, *Anal. Chim. Acta*, **480**, 275 (2003).
6. C. G. Cooney, B. C. Towe and C. R. Eyster, *Sensor. Actuat. B Chem.*, **69**, 183 (2000).
7. A. Mills, A. Lepre and L. Wild, *Sensor. Actuat. B Chem.*, **38-39**, 419 (1997).
8. A. Mills, Q. Chang and N. McMurray, *Anal. Chem.*, **64**, 1383 (1992).
9. B. H. Weigl and O. S. Wolfbeis, *Sensor. Actuat. B Chem.*, **28**, 151 (1995).
10. B. H. Weigl and O. S. Wolfbeis, *Anal. Chim. Acta*, **302**, 249 (1995).
11. R. Ali, S. M. Saleh, R. J. Meier, H. A. Azab, I. I. Abdelgawad and O. S. Wolfbeis, *Sensor. Actuat. B Chem.*, **150**, 126 (2010).
12. B. H. Weigl and O. S. Wolfbeis, *Anal. Chem.*, **66**, 3323 (1994).
13. C.-H. Yu, C.-H. Huang and C.-S. Tan, *Aerosol Air Qual. Res.*, **12**, 745 (2012).
14. R. Sanz, G. Calleja, A. Arencibia and E. S. Sanz-Pérez, *Appl. Surf. Sci.*, **256**, 5323 (2010).
15. X. Xu, S. Song, J. M. Andresen, B. G. Miller and A. W. Scaroni, *Energ. Fuel*, **16**, 1463 (2002).
16. J. Fujiki and K. Yogo, *Energ. Fuel*, **28**, 6467 (2014).
17. R. B. Vieira and H. O. Pastore, *Environ. Sci. Technol.*, **48**, 2472 (2014).
18. A. Dibenedetto, M. Aresta, C. Fragale and M. Narracci, *Green Chem.*, **4**, 439 (2002).
19. A. Zhao, A. Samanta, P. Sarkar and R. Gupta, *Ind. Eng. Chem. Res.*, **52**, 6480 (2013).
20. Z. Horak, J. Kolarik, M. Sipek, V. Hynek and F. Vecerka, *J. Appl. Polym. Sci.*, **69**, 2615 (1998).
21. A. Joiner, *J. Dent.*, **32**, 3 (2004).
22. T. Tsukatani, H. Katano, H. Tatsumi, M. Deguchi and N. Hirayama, *Anal. Sci.*, **22**, 199 (2006).
23. D. Heger, J. Klanova and P. Klan, *J. Phys. Chem. B*, **110**, 1277 (2006).
24. H. Petersen, T. Merdan, K. Kunath, D. Fischer and T. Kissel, *Bioconjugate Chem.*, **13**, 812 (2002).
25. L. Y. Qiu and Y. H. Bae, *Biomaterials*, **28**, 4132 (2007).
26. S. Wen, F. Zheng, M. Shen and X. Shi, *J. Appl. Polym. Sci.*, **128**, 3807 (2013).