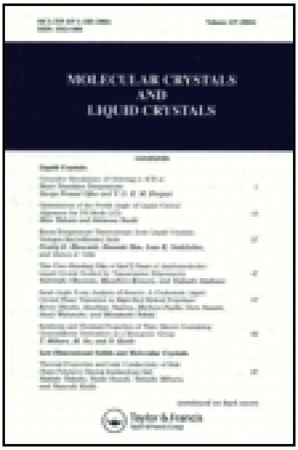

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Applications of pH sensor Using a Covalent Bond Indicator Based on Containing Functional Group Copolymer

Eun-Hee Kang [a], Jin-Kyoung Ham [a], Jong-Min Shim [a], Jin-Kook Lee [a] & Mi-Ra Kim [b]

[a] Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

[b] Department of Polymer Science and Engineering and Center for Plastic Information System, Pusan National University, Busan, Korea

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Eun-Hee Kang
Jin-Kyoung Ham
Jong-Min Shim
Jin-Kook Lee
Department of Polymer Science and Engineering, Pusan National University, Busan, Korea

Mi-Ra Kim
Department of Polymer Science and Engineering and Center for Plastic Information System, Pusan National University, Busan, Korea

The purpose of this study was to immobilize copolymer that is able to covalent bonding with pH indicator. The pH sensitive polymers were synthesized with copolymers that are consisted of acryloylamino acid and chloroalkyl acrylate with MMA to get the optical fiber matrix. Fluoresceinamine indicator, containing amino group was immobilized covalently on prepared copolymers. The prepared pH sensing copolymers were measured sensitivity by UV-Visible spectroscopy. The pH-dependent value of copolymers was examined in the pH range of 2.00 ~ 12.00 HCl/NaOH solution at room temperature. As the length side chain and MMA molar ratio of the copolymers increases, the intensity decreases. Compared with imine group of copolymer-dye derivatives, amide group derivatives have a bathochromic shift on the UV-Visible spectrum.

Keywords: MMA copolymer; pH sensor; pH-sensitivity dye; physiological pH range

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Address correspondence to Jin-Kook Lee, Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea. E-mail: leejk@pusan.ac.kr

INTRODUCTION

The pH intensity in tissue and blood vessels of human is desirable in a wide variety of clinical diagnostic studies. Despite the important parameter of pH measurement, the development of micro-pH electrode has the disadvantage of being rigid, no-disposable, and requires a reference electrode and electrical connection. On the other hand, fiber-optic chemical sensors (FOCS) using optical properties can offer several advantages over traditional sensors. The measurement can be performed directly in the sample without electromagnetic interference. They can also be miniaturized and the multiplexed signal can be transmitted over the long distances without significant loss to realize the remote area detection [1,2]. The One challenge in developing FOCS is to immobilize pH sensing agent in optical fibers, which measures the hydrogen ion activity. The pH sensor have been designed and developed which are available for tissue and blood pH measurements in the physiological range of pH $6.8 \sim 7.4$ [3].

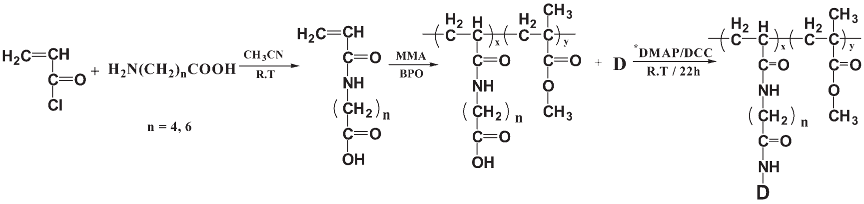
In the device of a typical fiber optic pH sensor, a reagent phase must be on the end of a fiber optic [4]. Mere attachment of the reagent phase to the surface of an optical fiber results in no detectable signal due to the limited area available. Interaction with analyte leads to a change in the optical properties of the reagent phase, which is probed and detected through the fiber optic. The reagent phase is polymer matrix or other supports on which a pH sensor based on an immobilized dye whose optical properties vary with pH [5,6]. The dye must be covalently attached to the polymer matrix or other supports with a spacer. Covalent binding of the sensing agent can minimize leaking out problem leading life-time improvement.

The function of the spacer is to keep the dye molecule at a sufficient distance from the polymer surface so that it measures a true pH response with the fast response and does not measure it the laminar sublayer close to the surface. The spacer ideally should be hydrophilic so that it would not coil towards the surface [7].

The purpose of this study is to immobilize copolymer which is able to covalent bonding with pH indicator, with an emphasis on the control of the spacer length between the dye molecule and polymer surface by using the different molecular, and to examine a difference of sensitivity functional group which is formed between the dye molecule and the polymer.

EXPERIMENTAL

Fluoresceinamine, aminoacids, chloroalkylalcohol and acryloyl chloride was used as received from Sigma-Aldrich without further



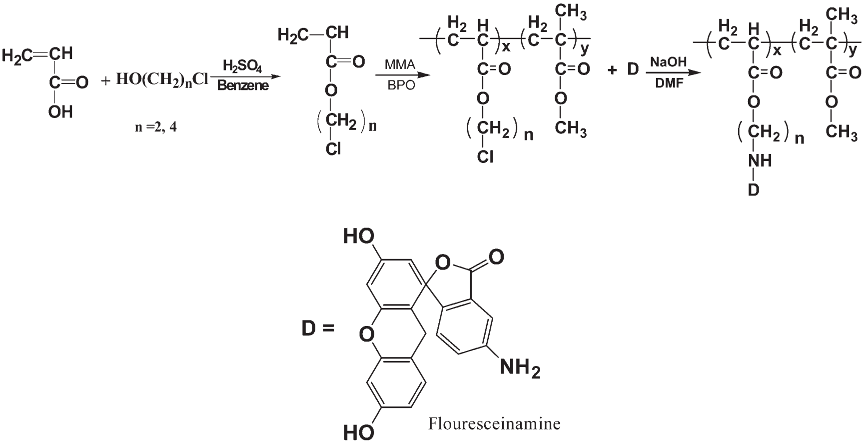
SCHEME 1 Synthesis of the copolymer for acryloylamino acid and MMA. DMAP: 4-Dimethylaminopyridine; DCC: 1,3-Dicyclohexylcarbodiimide.

purification. Methylmethacrylate (MMA) was obtained from Acros Chem. and used after purification with NaOH(aq) (10%, w/v) and distillation under reduced pressure.

FT-IR spectra was used to JASCO 460 Plus spectrometer using a KBr pellet, and ^{1}H-NMR spectra were recorded on a Varian 300 MHz. UV-Visible spectra of intensity were taken on a UVIKON 860 spectrophotometer. ACCMET model 10 pH meter was used to monitor pH in the tested solution.

Acrylate derivates were synthesized as shown in Scheme 1 and Scheme 2. Radical copolymerization by MMA was carried out in 1,4-dioxane at 70°C with BPO as a thermal initiator. The copolymers were purified by precipitation from filtered methanol, and dried under vacuum at room temperature.

A wide range of solution covering pH from 2.6–11.8 was prepared with de-ionized water using of hydrochloric acid (0.1 M) and sodium



SCHEME 2 Synthesis of the copolymer for chloroalkyl acrylate and MMA.

hydroxide (0.1 M). The dye-copolymers were made into concentration of 10^{-1} M in DMF solution. As the pH of the solution varies, optical absorption peak was taken measurements with UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

The structure of monomers, copolymers and copolymer-dye derivatives were characterized by various instrumental methods such as ^{1}H-NMR, FT-IR, and UV-Visible spectroscopy. In the first place, the FT-IR spectrum of monomers were able to find the strong carbonyl bond at 1649 cm^{-1} in amide group and the carbonyl stretching vibration at 1731 cm^{-1} in ester group, disappearing of $-$OH peak at 3400 cm^{-1}. The copolymers were found from the result that a peak of vinyl group (C=C, *sp*^{2} streching) disappeared from 3100 cm^{-1} in the FT-IR and $5 \sim 6$ ppm in the ^{1}H-NMR spectrum. The FT-IR spectrum copolymer indicators were found out the bending of aromatic ring at 1630 cm^{-1}and and 1447 cm^{-1}and $-$OH peak of alcohol at 3442 cm^{-1}.

The pH responses obtained for the fluoresceinamine dye immobilized in the copolymers in solution are shown in Figure 1. Chloroalkyl acrylate copolymer derivatives indicator have been a maximum absorption band at 491 nm that is associated with the deprotonated form of the dye. Contrary to theirs, acryloylamino acid copolymer derivatives indicator were found at 530 nm. The reason why acryloylamino acid copolymer indicator derivatives have got bathochromic shift is that between polymer and dye indicator have influence on

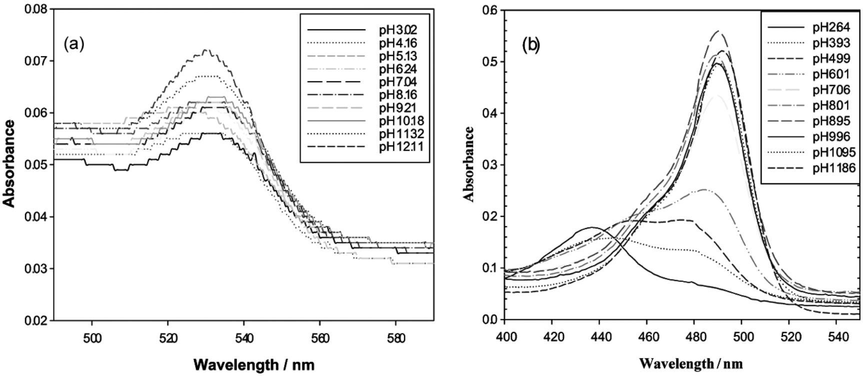


FIGURE 1 Absorption spectra of the sensor dye immobilized in copolymer for several pH values: (a) poly(MMA-co-acryloylaminobutylate) fluoresceinamine; (b) poly(MMA-co-2-chloroethyl acrylate) fluoresceinamine.

delocalization of electron by increasing of conjugation. Additionally, when the solution pH increases, the increase of responded absorption at 491 nm and 530 nm was observed individually. It is occurred when the dye makes the deprotonated form. Also it is shown that the absorbance of the sensor dye immobilized in a short chain is higher than that of the sensor dye immobilized in a long chain (Fig. 2). Based on this result, we can predict that as the chain length of the copolymer is longer, the absorbance intensity is weaker. To put it more concretely, as increasing side chain length seems to be decrease reactivity about MMA.

We varied the molar ratio of the MMA and acrylate monomers in the copolymerization from 9:1 to 1:9 (MMA: chloroalkyl acrylate, MMA: acryloylamino acid). The response curve of the absorbance is shown in Figure 2. As the molar ratio of MMA increases, the absorbance intensity decreases as expected. It clearly shows that the sensing dye is the attached fluoresceinamine and the quantity of the sensing dye affects the intensity.

The pK_a of the immobilized copolymer derivatives indicator were calculated by the change of absorbance at 491 nm and 530 nm with pH respectively. In case of chloroalkyl acrylate copolymer derivatives indicator, the absorbance changes gradually in pH region of 2.5–5.0. In pH region of 5.0–8.0, the absorbance changes rapidly with the pH. From this calibration curve, we can conclude that the immobilized fluoresceinamine has an average pK_a of 6.7 that is in the physiological pH range. The absorbance change is observed from 2.0 to 12. Because of large change by absorbance in pH region of 5.0–8.0, it is possible to measure blood pH with chloroalkyl acrylate copolymer derivatives

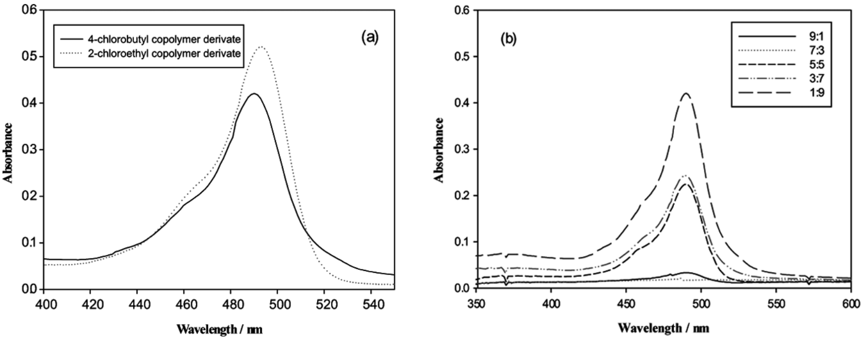


FIGURE 2 There is UV-Visible absorption spectrum; (a) as the chain length of the copolymer in the feed molar ratio MMA:chloroalkyl acrylate, 9:1; (b) as the feed molar ratio MMA and 4-Chlorobutyl acrylate.

indicator. On the contrary, acryloylamino acid copolymer derivatives indicator have an average pK_a of 8.9. It is presumed that bulky volume of molecule and limited reactivity with MMA has an effect on the reaction.

CONCLUSIONS

The pH sensing materials had been prepared by a combination of acrylate monomers and fluoresceinamine. We investigated the effect of alkyl length in copolymers-indicator. As the length of side group increases, the absorbance decreased. As the alkyl chain and MMA molar ratio of the copolymer increases, the intensity decreases. Compared with imine group of copolymer-dye derivatives, amide group derivatives have a bathochromic shift on the UV-Visible spectrum.

These results led us to the conclusion that we can control the intensity of the sensing dye. This study will be to provide measurements for pH sensor matrix in devices in the future.

REFERENCES

[1] Venetka, A. I. & David, R. W. (1993). *Biotechnology*, *11*, 726–729.
[2] Arwld, M. A. (1992). *Analyt. Chem.*, *64*, 1015–1025.
[3] Edward, B. (1992). *IEE Trans. Biochem. Eng.*, *39*(5), 531–537.
[4] Dafu, C., Qiang, C., Jinghong, H., Jinge, C., Yating, L., & Zemin, Z. (1993). *Sens. and Actu. B*, *12*, 29–32.
[5] Kostov, Y. & Neykov, A. (2000). *Analy. Lett.*, *33*(3), 413–423.
[6] Jin, Z., Su, Y., & Duan, Y. (2000). *Sens. and Actu. B*, *71*, 118–122.
[7] Pavies, M. L., Murphy, S. M., Hamilton, C. J., & Tighe, B. J. (1992). *Biomaterial*, *13*(14), 991–999.
[8] Baldini, F. (1998). *SPIE; Chemical, Biochemical, and Environmental Fiber Sensors*, *X*, 2–9.
[9] Park, S. Y. & Bae, Y. H. (1999). *Macromol. Rapid. Commun.*, *20*, 269–273.
[10] Lin, J. & Brown, C. W. (1997). *Trends in Analytical Chemistry 16*(4), 200–211.