Research of pH-sensitive functional material

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A new functional material was developed for pH chemical sensor. This material, which was made by polymer polymerization technique, was synthesized with copolymer materials. pH response character of the functional material was investigated. The result shows that this pH-sensitive functional material covers the pH range between 0 and 3.0 at the optimum proportion.

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Porous optical fiber sensors are attracting considerable interest recently. A unique porous glass fiber is used for use in fiber optical chemical sensors had been developed. In this approach, a small section of borosilicate glass fiber was phase separated by heat treatment, the boron-rich phase was leached out and an interconnected silica-rich porous skeleton fiber remained. And the porous glass segment can be sensitize by introduction of colorimetric chemical agents or indicators. This porous glass optical fiber sensor has been developed for the determination of ammonia, humidity and pH. However, the porous glass optical fiber required hard and careful techniques during fracture and application. Zhou Quan et al and our works presented an extension of the porous fiber approach into an all-polymer sensitive sensor for use in ammonia gas sensing. The use of plastic optical fibers instead of glass fibers offers many advantages, such as greater flexibility, high resistance to impact and vibration, larger numerical aperture, easier treatment of fiber ends and easier connection. That the plastic optical fiber can switch between hydrophilic and hydrophobic character due to its different polymerization material extends their applications greatly. Moreover, their lower cost and perfect biocompatibility make them suitable for biomedical applications.

In this work, we make use of Eosin as fluorescent indicator, methylacrylate as monomer, diethylene glycol dimethacrylate as cross-linking reagent, heptane as inert solvent. pH-sensitive functional material was synthesized by polymer polymerization technique. The sensitive material was uniform transparency, flexibility and easy to handling. pH response character was investigated in this paper. The result shows that this pH-sensitive functional material covers the pH range between 0 and 3.0 in solution.

Experimental

Chemicals and Instruments

970CRT fluorescent spectrophotometer (General manufactory of Shanghai analysis apparatus), pH5-2 model pH meter (Shanghai leichi Instrument factory of China).

Methylacrylate(C.R., Shanghai chemical reagent corp. of China medicine group), diethylene glycol dimethacrylate(A.R., Sigma), Eosin(A.R., Shanghai chemical reagent division in china), heptane(C.R., Zhongshan Shiji chemical factory in china), 2,2'-Azo-bis-iso-butyronitrile(C.R., the fourth reagent factory of shanghai in china). Buffer solutions in use were calibrated by pH meter. All other reagents were analytical reagent-grade. All aqueous solutions were prepared using doubly de-ionized distilled water.

Prepare of pH-sensitive functional material

Stopper should be removed from polymer material methylacrylate and diethylene glycol dimethacrylate before polymer. Methylacrylate, diethylene glycol dimethacrylate, Eosin ethanol solution and heptane in appropriate proportion were mixed evenly. 2,2'-Azo-bis-iso-butyronitrile was dissolved in the stock solution. N2 was then imported into the stock solution to remove O2 dissolved. The stock solution was injected into a 15-cm length and 1000um in diameter glass capillary. The filled glass capillaries were sealed by silicone glass sealant. When the final seal was made, it was essential to ensure that the capillary tubes were virtually free of air. After the silicone glass sealant was dry, the capillaries were then placed in an oven at 41 °C for 48h for polymerization to take place. The temperature was then gradually raised to 85-90 °C and held at this temperature for 10h to complete the polymerization. After polymerization, the uniform transparent plastic polymers were pulled out of the glass capillaries. Finally, the plastic polymers were put in acetone solution to remove any remaining inert solvent and superfluous indicator.

Fluorescence measurement

We designed a simple set (as fig.1) to cater corner fix pH-sensitive functional material in quartz cell. So that it can be placed in fix shelf in fluorescent spectrophotometer. Fluorescent intensity was measured at λex,500nm in buffer solution with different pH.
Results and Discussion

Preliminary polymerization temperature and initiator content

Synthesis of polymer material related to the preliminary polymerization temperature and polymerization initiator. When the temperature was too low or the initiator was insufficient, polymerization cannot take place. If the temperature was too high or the initiator was superfluous, the velocity of synthesis was rapid. That caused the polymer to become opaque due to its low molecular weight. 0.013 g/mL \( 2,2\)-Azo-bis-isobutyronitrile in stock solution and 41-43°C as the preliminary temperature were applied in our experiment.

Proportion of monomer and cross-linking reagent

If there was not cross-linking reagent in the stock solution, the polymer arose serious swelling in solution and that caused indicator Eosin to leak speedily out of the polymer. In pH buffer solutions response curves of pH-sensitive functional material with different proportion of monomer and cross-linking reagent were showed in fig.2. The response sensitivity for pH in solution decreased and the response time lengthened while the content of cross-linking reagent in functional polymer increased. When the proportion (v/v) of monomer and cross-linking reagent reached 1:1 (in fig.2 curve 4), the functional polymer material hardly responded to pH in solution due to its hydrophobic increasing. Taking sensitivity and response time into account, in the optimal proportion (v/v) 3:1 of monomer and cross-linking reagent was chose in our experiment.

Fluorescence spectrum

Fluorescence spectrums of Eosin in different circumstance were show in fig.3(on the left of fluorescent spectrum there were scatter spectrums of the pH-sensitive functional polymer). The fluorescent wave of Eosin solution was 549nm in pH 3.0 buffer solution and the fluorescent wave of Eosin was 552nm and 566nm embedded in functional polymer with methylacrylate and methyl methacrylate as monomer respectively in pH 3.0 buffer solution. From the spectrum graph, we can draw a conclusion that different circumstance indicator Eosin was at made its max emission wave shift.

![Fig.3 Fluorescent spectrum of indicator Eosin in different circumstance](image)

1. Eosin solution in pH 3.0 buffer solution  
2. Eosin embedded in functional material with methylacrylate as monomer in pH 3.0  
3. Eosin embedded in functional material with methyl methacrylate as monomer in pH 3.0 buffer solution

Response curve

Fluorescent spectrums of pH-sensitive functional material in pH 1.0 and pH 3.0 buffer solutions were showed in fig.4 (on the left of fluorescent spectrum there were scatter spectrums of the pH-sensitive functional material). Fig.5 illustrated the pH response between pH 1.0 and pH 15.0 when exciting at 500nm and monitoring at 552nm. A near linear relationship between fluorescent intensity of pH-sensitive functional material and pH between 0 and 3.0 is observed.

![Fig.4. Fluorescent Spectrum of pH-sensitive functional polymer in buffer solution](image)

1. pH 1.0, 2. pH 3.0

Inert solvent

The experiments showed that the response time between the same two pH buffer solutions of pH-sensitive functional material, of which there was not inert solvent added in stock solution, was much longer than that of the functional polymer having inert solvent in the stock solution. In our experiment, heptane and tetrachloromethane were tested as inert solvent. Heptane was superior to tetrachloromethane for the response time of the pH-sensitive functional polymer with heptane as inert solvent was shorter than that of the functional polymer with tetrachloromethane as inert solvent, the response time got shorter while the content of inert solvent increased. However the leaking of indicator become more serious simultaneously. If the content of inert solvent was too superfluous, the polymer material went so far as to become opaque. So suitable proportion of inert solvent should be chose. 20%(v/v) of heptane in the stock solution was chose in our experiment.
Reversibility
Change in the fluorescent intensity of pH-sensitive functional material for the three pH3.0, 2.0 and 1.0 is showed in Fig. 6. The functional material has reversible response to pH in solution.

Leakage
Leakage of indicator influenced directly on the lifetime of chemical sensor. The pH-sensitive functional material was dipped in pH1.0 and pH3.0 buffer solutions for 96h respectively, there were no fluorescent signal observed under the same detection condition of calibration curve. So the leakage of indicator Eosin can neglect during the detection.

All-polymer sensitive sensor for pH was developed. By polymer polymerization technique, pH-sensitive functional material was synthesized with Eosin as fluorescent indicator, methylacrylate as monomer, diethylene glycol dimethacrylate as cross-linking reagent, heptane as inert solvent. pH response character of this functional material was discussed in this paper. The result shows that this pH-sensitive functional material covers the pH range between 0 and 3.0 in buffer solution when exciting at 500nm and monitoring at 552nm.

Coupling the pH-sensitive functional material to optical fiber sensor is under progress in our laboratory; further works should be focus on the investigation of immobilizing other indicators by this method, extending the linear response range and reducing the response time.

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