Selective Recognition of Chloroacetic Acids by Imprinted Polyaniline Film

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ABSTRACT: A novel conductive imprinted polyaniline (PAN) film is prepared by adding template during the PAN film preparation. Monochloroacetic acid (MCA) and trichloroacetic acid (TCA) were used as templates. The conductivity of imprinted PAN films was measured by the four-point probe method. The conductivity changes of imprinted PAN films were compared to reference PAN reflecting the MCA and TCA specific sites on the surface of PAN films. The conductivities were linearly dependent on the template concentrations, and linear calibration curves were obtained in the range 1–30 and 1–40 ppm of the MCA and TCA, respectively. Excellent method reproducibility (standard deviation 0.04 S/cm^{-1}) was observed for the determination of 15 ppm MCA. The effect of various factors on preparation, properties, and recognition effects of the imprinted PAN films was investigated. The best electrical and mechanical properties were obtained with 7×10^{-4} mmol MCA as a template and doping agent. The measurements are carried out under room temperature, and the maximum conductivities are reached after about 10 and 20 min for reference and imprinted PAN film, respectively. Selectivity experiments were carried out with standard MCA, TCA, and five analogs (dichloro-, dibromo-, and monobromoacetic acid) in water. The results exhibited a good selectivity for the templates compared to structurally related compounds. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 292–298, 2011

Key words: molecular imprinting; conducting polymer; haloacetic acids; polyaniline

INTRODUCTION

During the last several years, conducting polymers have gained substantial attention due to their potential applications in the electric and electronic industry. Polyaniline (PAN) has been the subject of several studies because of its chemical and oxidative stability, ease of preparation, stable electrical conduction mechanism, good redox properties, and easy dopability with a range of dopants.[1,2] Conducting PAN may also be used as sensitive layers in chemical sensors; therefore, the changes in the electronic properties of PAN in response to different chemical and biological analytes have been studied.[3,4] It is of interest to study the electronic properties of PAN particularly for its possible application in the development of sensitive and specific personal monitoring sensors, which are capable of detecting such toxic vapor and gas.[5–7] Despite the various advantages of conducting polymer, no commercial systems are yet developed because of the remained poor selectivity and reversibility of these materials.[8]

Molecular imprinting is an effective strategy for the preparation of polymer materials having recognition sites with high affinity for a target molecule (template).[9–12] Unique properties of these materials such as excellent stability, ability to function in various media, antibody like recognition capability find applications in diverse areas like separation, solid-phase extraction, antibody mimics, and sensors.[13–16] The main approach for obtaining molecularly imprinted polymers (MIPs) is the use of a prearranged template-polymerizable monomer complex (either by covalent or not covalent interactions). After polymerization in the presence of an excess of a crosslinking agent, the complex is captured into a rigid, highly crosslinked macroporous polymer. As a result of extensive crosslinking, it is extremely difficult to fabricate MIPs as films with adequate mechanical features. Furthermore, time to attain equilibrium in MIPs is long. These aspects limit the applications of MIPs in sensor's technology where a fast response is mandatory. In the recent years, there have been several approaches and strategies to coat thin layers of imprinted polymers on various substrates, such as electrodes and glass slides.[17–24] More recently, several authors have shown that conjugated polymers are promising materials for MIP formation, and artificial binding sites can be imparted for molecules of interest by simply adding them as templates during the polymerization.[25,26] PAN is one of the most important members of the conducting polymer

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family and can be easily synthesized, either chemically or electrochemically, in good yield. Therefore, numerous studies on PAN films have been carried out with the intention of developing recognition ability toward template molecules.[27–31]

Chloroacetic acids (CAAs) are formed on the addition of chlorine to water for disinfection purposes[32–34] and through C2-chlorocarbon and chlorofluorocarbon replacement compounds in various industrial applications.[35] In addition, CAAs are used as herbicides and defoliants and chemical intermediates in the production of carboxy-methyl cellulose, ethyl chloroacetate, glycine, synthetic caffeine, sarcosine, thioglycolic acid, EDTA, some vitamins, dyes, and drugs.[36] CAAs tend to accumulate in surface water and pose threats to humans and the ecosystem due to their toxicity and high stability. Many researches have demonstrated that CAAs are also carcinogenic to humans.[37] Various instrumental methods have been reported for the determination of CAAs. These methods are time consuming and suffer the shortcomings of certain interferences and expense. Fast and sensitive screening methods could be an essential complement to these sophisticated instrumental methods. Recently, conductometric sensors based on CAA-imprinted polymers specific to the group of haloacetic acids (HAAs) have been developed by Suedee et al.[38,39] They demonstrated that the sensor based on CAA-imprinted polymer is a fast and sensitive screening method of HAAs in drinking water.

However, there is a demand for a simple and a versatile method for the determination of them in trace amounts. An imprinted PAN layer would be appropriate for such applications and after binding step, and the molecules can be detected using measurement of conductivity changes with a four-probe device. An approach of this kind is yet to be reported. In this work, we reported the feasibility of preparation of an imprinted PAN film by adding templates during the film preparation. This seems to be a novel and easy way to create affinity sites selective to the template. We have investigated the monochloroacetic acid (MCA) and trichloroacetic acid (TCA) sensing characteristics of the imprinted films through electrical conductance measurements using a linear four-point probe technique. It is demonstrated that this method exhibit high sensitivity, reversibility, and reproducibility for MCA and TCA.

EXPERIMENTAL

Reagents and materials

All chemicals were of analytical grade and were purchased from Merck or Fluka. Aniline was purified by refluxing with 10% acetone for 10 h, and then it was acidified with HCl. It was extracted with Et2O until colorless. Chloroform and *N*-methylpyrrolidone (NMP) were dried on silica gel and distilled over phosphoroxide in the presence of nitrogen gas. Stock MCA and TCA solutions of 0.05*M* were prepared. Standards of working solution were made by appropriate dilution daily as required.

Instrumentation

Electrical conductivity of the PAN films was measured by a four-probe device (home-made). The spectroscopic studies in the infrared region were performed from PAN films in the range of 400–4000 cm^{-1}. A Shimadzu Model 8400S FTIR spectrometer was used for these measurements. The number of scans was 20. The surface features of imprinted PAN films were characterized by scanning electron microscopy (SEM). A Phillips XL-30 SEM was used for this purpose. A thin layer of gold was coated onto the surface before the visualization.

Preparation of the imprinted PAN films

PAN is mostly synthesized by aniline oxidation either with a chemical oxidant (chemical route) or through electrochemistry.[26] The chemical oxidation is adopted in this report for its synthesis. Briefly, 0.01 mol (1.03 g) aniline was dissolved in 10-mL 1*M* hydrochloric acid. Then, 0.01 mol (2.53 g) ammonium persulfate (APS) was dissolved in 10-mL distilled water. The experimental part consists of slowly adding (even drop by drop) the aqueous APS solution to the aniline/HCl solution under constant stirring, both solutions being precooled to 0°C. The mixture was kept at 0–5°C for 5 h. The formed precipitate is removed by filtration and washed repeatedly with methanol and water until there was no color in filtrate. Then, the precipitate is dried under vacuum for 24 h.[40] The obtained material is polyemeraldine salt, polyemeraldine hydrochloride (PANHCl), green colored. To obtain polyemeraldine base, PANHCl is treated in an aqueous ammonium hydroxide solution 0.1*M* for about 15 h. The obtained powder is washed and dried as described earlier. Then, 0.1 g PAN powder was added to 10 mL of NMP solution and magnetically stirred at room temperature. The resulting solution was prefiltered twice through a Buchner funnel using Whatman no. 541 filter paper to remove large particles. About 0.2 mL of this solution was mixed with 0.7 mL $1 \times 10^{-5}M$ MCA (or TCA) solution and diluted to volume (2 mL) with NMP. Imprinted PAN films (50–100 μm thick) were prepared by casting the solutions onto a preheated glass slide, which was then placed in an oven (50°C) with 10 mmHg vacuum condition. In general, slower drying gave film with more uniform thickness. Dried imprinted PAN films

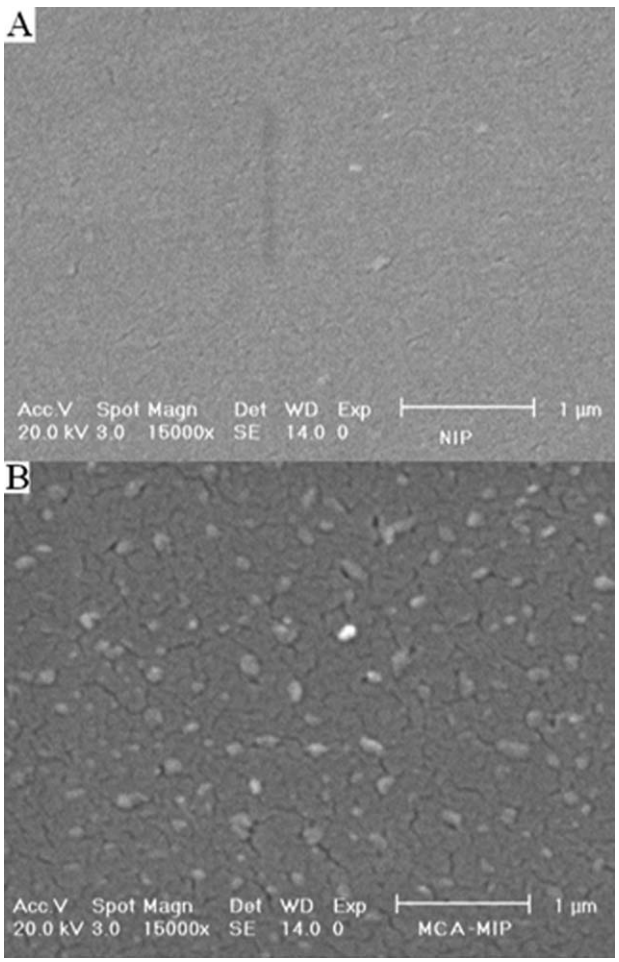

Figure 1 Scanning electron micrographs of (A) nonimprinted PAN, (B) imprinted PAN.

were removed from the glass by immersion in water. A nonimprinted PAN was prepared in the same conditions without the template. The conductivity of imprinted PAN films measured with the four-probe method was about 1.5 S/cm. Polymer films were extracted several times with chloroform. The imprinted PAN films were considered clean if the conductance was lower than 0.01 S/cm. Once complete, the polymer films are ready for testing.

Interaction of the imprinted PAN films with the templates

A series of standard solutions of MCA and TCA were prepared in double-distilled water (0–45 ppm). Polymer strips, having a size of 2 × 2 cm^2, were placed in these solutions. The uptake of the template molecules by the imprinted PAN films was investigated by measuring the conductance of polymer strips at regular time intervals. The modification process was carried out in triplicate to assess the reproducibility of the methodology. The conductance was measured after drying the polymer strips in a vacuum oven at 50°C for 5 min. Nonimprinted PAN strips were also subjected to the same standard solutions to serve as control.

RESULTS AND DISCUSSION

PAN-imprinted preparation

The conducting mechanism of PAN is induced either by the oxidation of the polyleucoemeraldine base or by the protonation of the polyemeraldine base. It is known that the polymerization leads to the formation of polymeric stretches containing up to 1000 or more *p*-phenyleneimine repeated units. The conducting form of PAN (doped with strong acids) is insoluble in organic solvents. Ordinarily, PAN is cast into films from the emeraldine base, or undoped, nonconducting form, from a dispersion of the powder in NMP. Scanning electron micrographs of nonimprinted and imprinted PAN are shown in Figure 1(A,B), respectively. The surface morphology of the imprinted PAN appears to be distinct from the surface characteristics of the blank PAN. The presence of the template molecule during the film preparation and its subsequent removal could be responsible for the alteration of the surfaces of nonimprinted and imprinted PAN.

Interaction of the acetic acids series and some other organic acid with the PAN is described in detail elsewhere.[41,42] The change in the spectral nature of PAN can be observed in the vibrational spectra based on changes in the position and shape of the characteristic IR bands of PAN. Figure 2 represents the FTIR spectra of PAN nonimprinted and imprinted PAN films. As can be seen, there are major vibrational bands around 832 (C—H out of plane), 1511 (C=C benzenoied ring stretch), 1596 (Quinoid

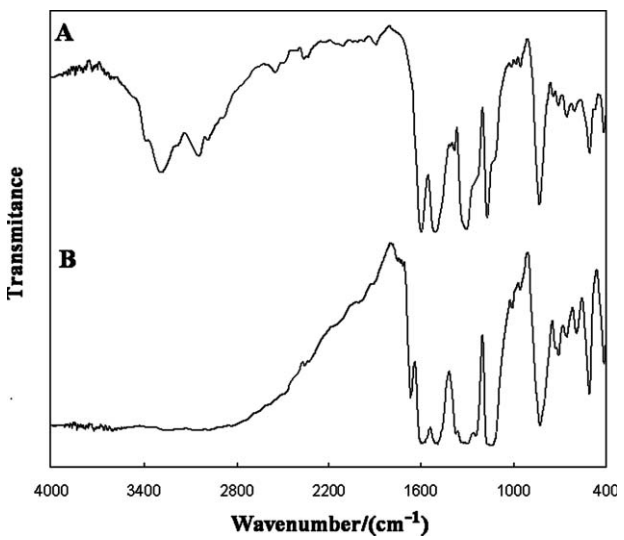

Figure 2 FTIR spectra for (A) reference PAN film and (B) MCA imprinted PAN film.

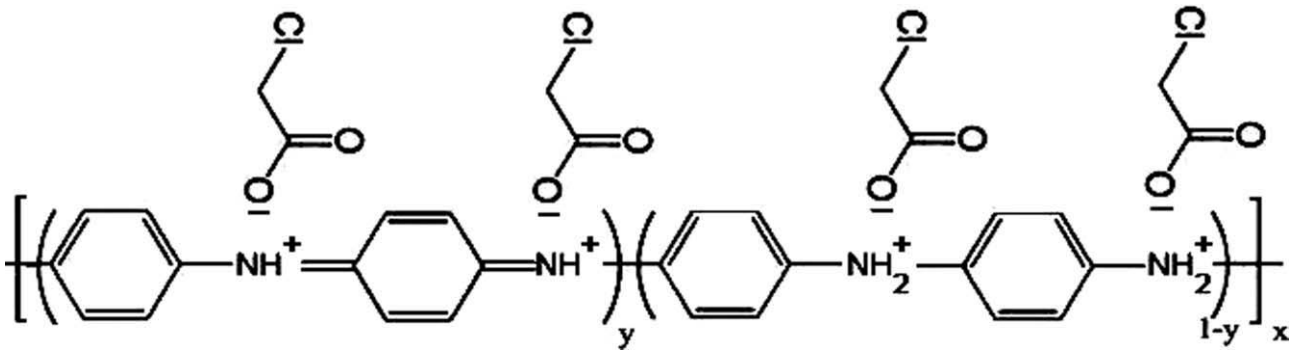

Figure 3 Schematic view of interaction between MCA and polyaniline.

C=N stretch), 3045 (C—H aromatic), and 3288 (N—H) cm^{-1} in the nonimprinted PAN film spectra [Fig. 2(A)]. The observed bands, characteristic of emarldine form of PAN, are in good agreement with the values reported in the literature.[43–45] As seen from Figure 2(B), the imprinting of PAN by MCAs results in broadening and increasing of intensity of the vibrational bands, which indicate interaction between MCA and PAN. The previous studies have been shown that the basic imine groups in the PAN structure are fully protonated when the film is cast from CAAs.[41] A schematic view of the structure of the imprinted PAN doped with MCA is shown in Figure 3. The creation of affinity sites for CAAs is assumed to be due to such interactions. We have also studied the effect of various factors on preparation, properties, and recognition effects of the imprinted PAN films. The obtained results are given below.

Effect of experimental parameters on imprinted PAN properties

Effect of template concentration on PAN film preparation

The imprinted PAN film preparation was carried out with varying MCA and TCA concentration, and the effect of concentration of the acids on mechanical properties and conductivity of the PAN films was examined. As shown in Figure 4 by increasing the mole of template, the conductivity of the PAN film increased due to doping effect of MCA. However, at high concentrations, the MCA stability of the imprinted PAN film decreased, and prepared films were brittle. The best electrical and mechanical properties were obtained with 7×10^{-4} mmol MCA as a template and doping agent.

Effect of time on template uptake

Figure 5(A) shows the conductivity dependence of the imprinted PAN film and the corresponding reference PAN on the MCA exposure time. It is seen that the conductivities of the films increase with similar rate. The similarity among the film conductivities in the initial times may be because only nonspecific adsorption of MCA is responsible for increasing the conductivity at this stage. The maximum conductivities are reached after about 10 and 20 min for reference and imprinted PAN film, respectively. It can be related to kinetics penetrate of template into cavities. However, conductivity in imprinted PAN film is considerably more than the reference PAN film. This shows that the enhanced conductance by the imprinted surface is indeed due the creation of affinity sites. The exposure time dependence of film conductivities was monitored for repeated exposure and removal of MCA.

Effect of experimental temperature

The influence of variation of the experimental temperature on the response of the reference and

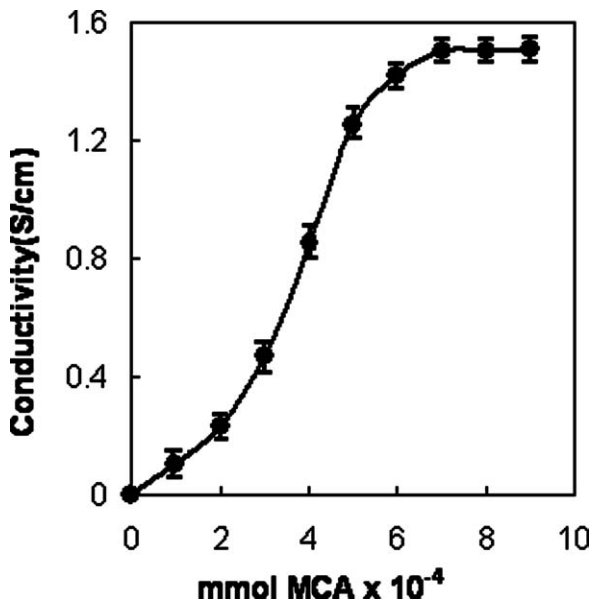

Figure 4 Variation of the electrical conductivity of imprinted PAN film with various MCA (template) concentrations. The error bar is the standard deviation of three measurements.

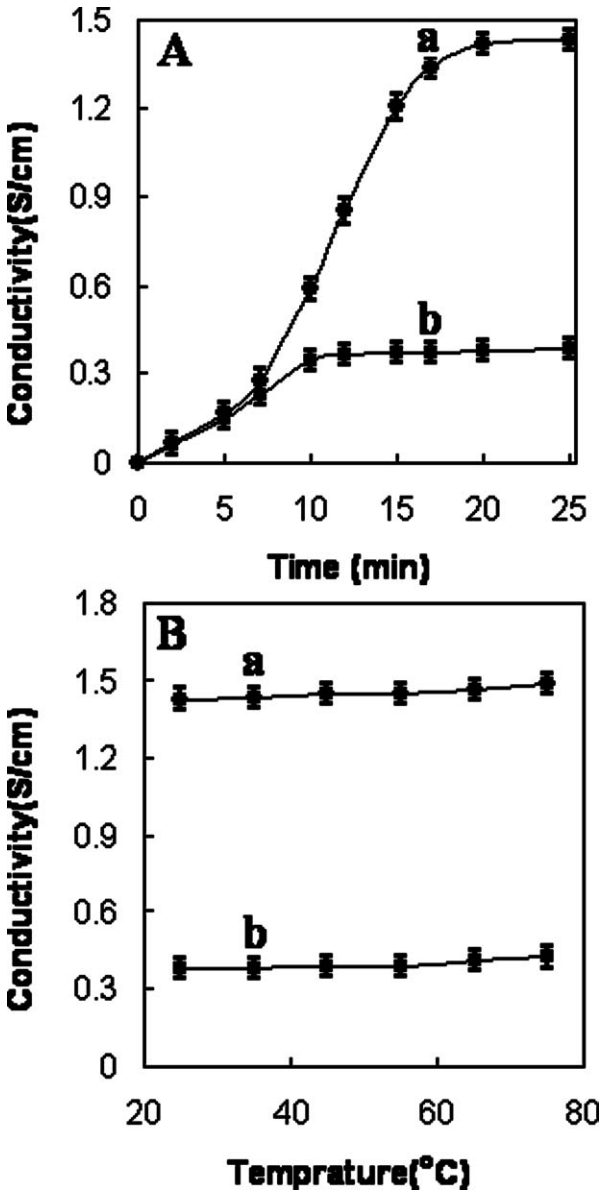

Figure 5 A: Time dependence of conductivity; (B) effect of temperature on the conductivity for: (a) MCA imprinted PAN film; (b) reference PAN film on exposure of MCA 30 ppm. The error bars represent the standard deviations of three measurements.

imprinted PAN film on exposure to MCA (30 ppm) was investigated over the temperature range of 25–75°C. As seen in Figure 5(B), the conductivities of imprinted and reference PAN film slightly increase with increasing temperatures. The result obtained in this study showed that temperature changes could not have strong influences on the sensitivity of the PAN films. Thus, measurements could be carried out under room temperature.

Effect of time on PAN films conductivity

We measured the evolution of the conductivities of the reference and imprinted PAN film for different periods after preparation. For this purpose, the washed polymer strips were subjected to MCA (30 ppm) during 20 min. Then, the conductivity changes of polymer strips at regular time intervals were measured. Figure 6 shows that the conductivity decreases faster in the reference PAN when compared with the imprinted PAN film. It is believed that the MCA as dopant species is adsorbed on the reference PAN film and is fully evaporated in 1 month, while penetrated MCA in cavities of the imprinted PAN is not easily removed and therefore negligible dedoping occurs with time. The results obtained show that electrical conductivity of the imprinted PAN film is not only considerably higher than of the reference PAN but also very stable over 3 months at room temperature. Similar results were obtained for imprinted PAN films with TCA.

Concentration dependence on conductivity

Variation of conductivities with concentration MCA and TCA for the reference and imprinted PAN films is shown in Figure 7. The polymer strips were incubated in a series of CAAs solutions with different concentrations (0–45 ppm). As can be seen from Figure 7, the reference and imprinted PAN films give signal responses primarily rising with an increase in the concentration of CAAs. Because of the high affinity of the specific binding sites in the imprinted PAN film, the conductivity response of the imprinted PAN films is higher than that of the reference PAN. At higher concentrations of CAAs, the responses of PAN films seem to be constant, which is probably explained by the saturation of the binding sites in the polymer

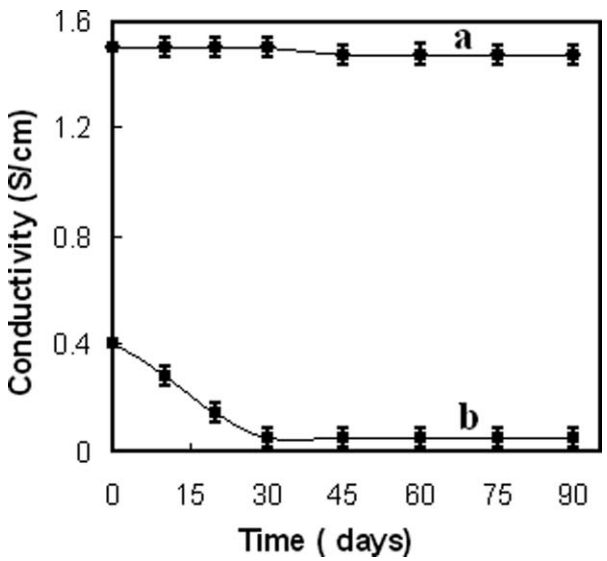

Figure 6 Conductivity over time for (a) MCA imprinted PAN film; (b) reference PAN film. The error bars are the standard deviation of three measurements.

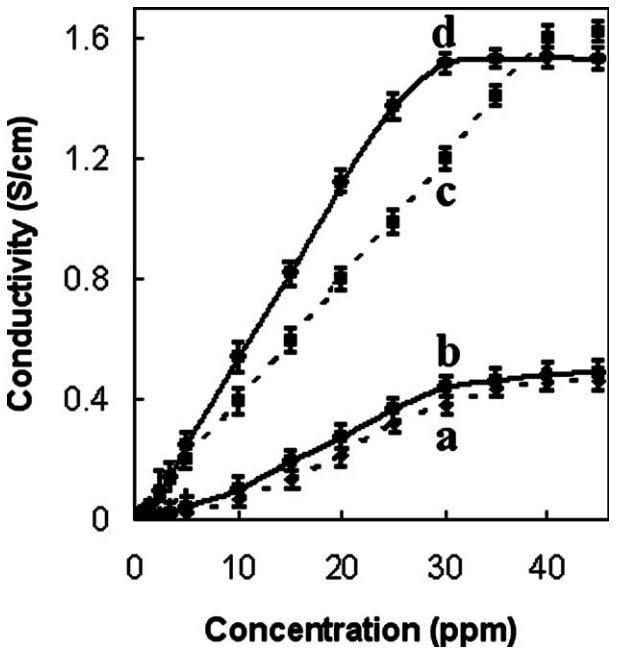

Figure 7 Concentration dependence of polymer strips to template standard solutions: (a) and (b) for reference films toward MCA and TCA standard solutions. (c) and (d) as (a) and (b) for MCA and TCA imprinted films, respectively. The error bars represent the standard deviations of three measurements.

strips. The calibration curves constructed from the conductance dependency provided reasonable results. There are linear relationships between the conductance of the imprinted PAN film and the concentrations of MCA and TCA between 1 and 30 and 1–40 ppm, respectively. The limit of detection as obtained according to $3S_b/m$ criterion, where m is the linear calibration and S_b were estimated as the standard deviation ($n = 5$) of the conductivity response for MCA was 0.5 ppm. The limit of detection for TCA using the TCA imprinted PAN film was found to be approximately 0.4 ppm.

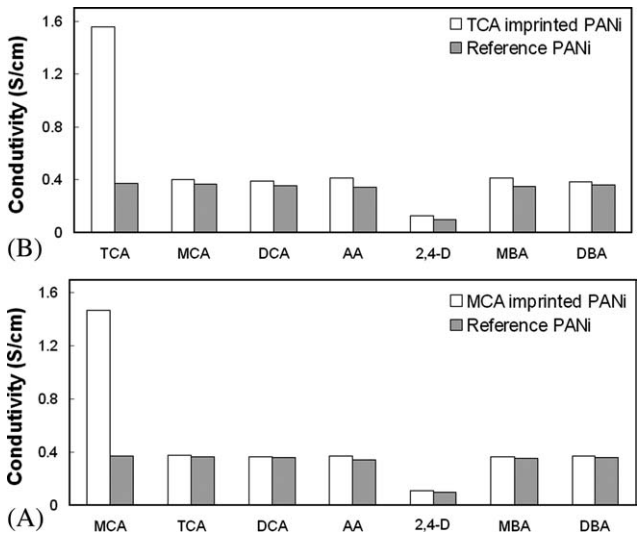

Figure 9 The conductivity response of (A) the MCA imprinted PAN film and (B) the TCA imprinted PAN film to several analogies. Measurements were carried out in the solution containing 30 ppm of the analogs.

Reproducibility and repeatability of imprinted PAN films

The reproducibility of the sensor was confirmed by the conductivity measurements of the imprinted PAN films from three independent film preparation under the same experimental conditions. The average conductivity for MCA (15 ppm) was 0.820 S/cm^{-1} with a standard deviation of 0.04 S/cm^{-1}. The repeatability of the sensor was examined at a MCA concentration of 30 ppm with the same imprinted PAN film. Also, the standard deviation for 10 cycles was less than 0.05 S/cm^{-1}. After each measurement, MCA could be removed from the MIP filmstrips by immersing the sensor in chloroform. With this washing treatment, the conductivity of polymer film was

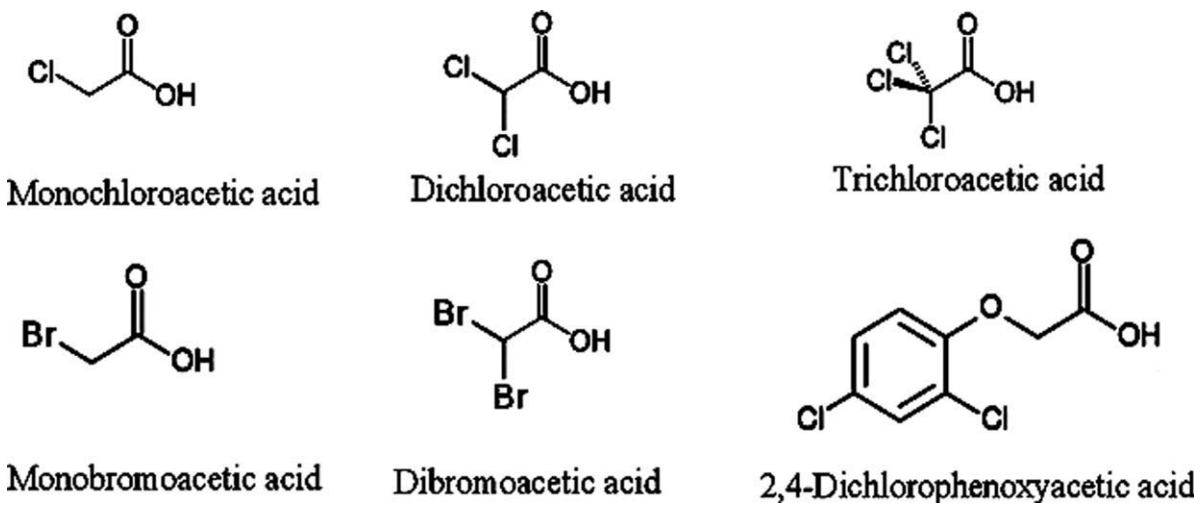

Figure 8 Structure of the investigated compounds.

easily returned to 0.01 S/cm^{-1}, and the sensor was recovered within 5 min. It was therefore confirmed that repetitive use is possible with this sensor.

Selectivity of imprinted PAN films

The effect of some structurally related HAA compounds such as dichloroacetic acid, monobromoacetic acid, dibromoacetic acid, and other compounds such as acetic acid and 2,4-dichlorophenoxyacetic acid (2,4-D), on the imprinted PAN, and reference films conductivity were examined (Fig. 8). The results of selectivity experiments are shown in Figure 9. As seen from Figure 9(A), the conductivities observed with both the MCA-imprinted PAN and reference films for potential interfering compounds are relatively little and similar together. The results show that the HAA analogs are capable of inducing changes in the conductivity of PAN films due to their adsorption and relative doping effect. On the other hand, the MCA generated significant changes in the electrical conductivity of MCA-imprinted PAN. Thus, MCA is better recognized than other HAA analogues. This also shows a definite imprint effect in the MCA-imprinted PAN film. Similar results were obtained for selectivity of TCA-imprinted PAN film [Fig. 9(B)].

CONCLUSIONS

The results summarized in this communication show that creation of affinity sites is possible when template is added during in the film preparation step. The sensor exhibits good sensitivity, selectivity, and reproducibility for MCA and TCA by virtue of the interaction between imprinted PAN-binding sites and templates. The HAA sensing capability of the imprinted PAN films is investigated. The filmstrips exhibited stable, reproducible, and eversible conductance changes in the presence of MCA and TCA in the 1–30 and 1–40 ppm range, respectively. The imprinted PAN films showed long-term mechanical and chemical stability. The methodology is simple, and imprinted PAN films could be used in sensing applications.

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