New Poly(*N,N*-Dimethylaminoethyl Methacrylate)/Polyvinyl Alcohol Copolymer Coated QCM Sensor for Interaction with CWA Simulants

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Ⓢ *Supporting Information*

ABSTRACT: A series of copolymers, namely, poly (*N, N*-dimethylaminoethyl methacrylate)/polyvinyl alcohol (PDMAEMA/PVA), have been obtained through emulsion polymerization. Then, a synthetic copolymer (PDMAEMA/PVA)-coated quartz crystal microbalance sensor (PC-QCM) has been developed to apply in evaluating the interactions between the copolymers and three chemical warfare agent (CWA) simulants, such as diethyl chlorophosphate (DCP), 2,2'-dichlorodiethyl ether (DCE), and dimethyl methylphosphonate (DMMP). The results from the QCM measurements indicate that the PDMAEMA/PVA copolymers not only directly degradate sarin simulants (DCP and DMMP), but also show obvious absorption in mustard gas simulant (DCE). In addition, the mass of degraded DCP by the copolymer is calculated on the basis of resonance frequency shifts (Δf) of quartz crystal in the QCM sensor, which may be applied to quantitatively evaluate the reactivity of PDMAEMA/PVA copolymers. Furthermore, the fluorescence of PDMAEMA/PVA copolymers in DMSO solution gradually quenched with the addition of DCP solution, which can be explained that the reactions take place between DCP and reactive groups of PDMAEMA/PVA copolymers. Thus, this PDMAEMA/PVA membrane may be a good candidate for the application in chemical warfare protective materials, and this new PC-QCM technique shows potential application in the rapid, real-time, and sensitive detection of the chemical warfare agents and hazardous chemicals.

KEYWORDS: *PDMAEMA/PVA, copolymer-coated QCM sensor, chemical warfare agent simulants, degradation, fluorescence*
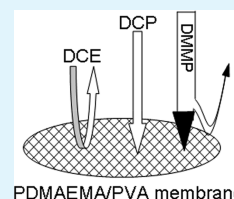
1. INTRODUCTION

A great many safety incidents caused by various hazardous chemicals and chemical warfare agents (CWAs) such as sarin and mustard gas occurred all over the world. Many scientists have focused on developing high-performance protective materials over the past decades,[1–3] in order to avoid the possible harm from these hazardous chemicals. In comparison with the traditional materials such as activated carbon, butyl rubbers, and active carbon fibers etc.,[4,5] the reactive polymer materials containing active groups, which may react with CWAs quickly, have attracted more considerable attention since the 1990s, because of the potential advantages such as lightweight, good selective permeation, as well as self-detoxifying toxic chemicals.[6] In the meantime, various technologies such as ^{31}P NMR,[7] UV–vis spectra,[8] total hydrocarbon analyzer equipped with FID detector,[9,10] etc., have been rapidly developed in the evaluation of protection performance for these reactive polymer materials.

Quartz crystal microbalance (QCM) as an ultrasensitive mass sensing device has widely been used to measure minor mass change in the recent years.[11,12] When placing a quartz crystal into alternating electric field, the minor mass change on the quartz crystal surface causes the frequency shift of the quartz crystal resonator. Thus, the change of mass can be calculated through Sauerbrey equation[13] based on the frequency shift of quartz crystal. Recently, some new QCM sensors modified with functional materials such as ZnO-MnO₂ nanofibers[14] and epoxy resin polymer[15] etc have been developed to detect CWA stimulants, for example diethyl chlorophosphate (DCP), dimethyl methylphosphonate (DMMP), and 2, 2'-dichloro-diethyl ether (DCE) etc. As these materials have unique physicochemical, electronic and surface properties, they may selectively bind with some CWA simulants through the coordination as well as weak interactions (hydrogen bonds and π–π stacking). In addition, QCM sensor technique has shown many advantages, such as fast response, real time, low detection limits and easy operation, compared to the other analytical methods for example GC, GC-MS, IMS, NMR, UV–vis spectra, etc.[16–22] Until now, the studies on degradation of chemical warfare agents and their simulants by using QCM sensors coated with reactive polymer materials have been rarely reported.

Addition of polyvinyl alcohol (PVA) into poly (*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) greatly enhances the hydrophilism, moisture penetrability, and film forming of the resulting copolymers (PDMAEMA/PVA).[23]

Herein, a new PDMAEMA/PVA copolymer membranes coated QCM sensor (PC-QCM) has been developed and applied in evaluating the interaction between these PDMAEMA/PVA membranes and chemical warfare agent simulants, such as DCP, DCE, and DMMP. The results obtained from QCM measurements reveal that these PDMAEMA/PVA copolymers-coated QCM sensors show different responses to three simulants, which have strong chemisorption to the sarin simulants (DCP and DMMP in this work), and show typically physical adsorption in the mustard simulant (such as DCE). Moreover, the reaction mechanism between PDMAEMA/PVA copolymers and DCP has been further investigated by the change of fluorescence spectra and ^{1}H NMR studies.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Apparatus. Polyvinyl alcohol (PVA) (95% hydrolyzed, average M.W. 95,000) was purchased from J&K Scientific Ltd. (N,N-dimethylamino)ethyl methacrylate (DMAEMA) was obtained from Zibo Chemical Factory (China Shandong). Diethyl chlorophosphate (DCP) and 2,2'- dichlorodiethyl ether (DCE) were bought from Beijing Ouhe Technology Co. Ltd. (China). Dimethyl methylphosphonate (DMMP) was obtained from Qingdao Haida chemical Co. Ltd. (China). The AT-cut quartz crystals (8 MHz resonant frequency, 0.5-mm thickness), covered with gold electrodes of 5 mm diameter on both sides, were bought from Chenhua Co. Ltd. (Shanghai, China). All other chemicals were obtained from commercial sources and used without further purification. IR spectra were recorded with a Perkin−Elmer Spectrum One spectrometer with KBr pellets in the range from 4000 to 400 cm^{-1}. Photoluminescence determination was carried out on a Hitachi F-2500 spectrophotometer at room temperature. ^{1}H NMR spectra were recorded using Varian 400 spectrometer (400 MHz) in DMSO-d^6 solution with TMS as an internal standard at room temperature.

2.2. Preparation of PDMAEMA/PVA Copolymer Materials. The preparation of PDMAEMA/PVA copolymer materials was carried out according to the modified emulsion polymerization method.[23] The mixture of DMAEMA (10 mL), potassium peroxydisulfate (0.09 g) as the initiator agent, sodium dodecylsulfate (SDS, 0.06 g), Span−80 (0.03 g), and deionized water (15 mL) was heated to 50 °C for 2 h under nitrogen atmosphere. Then, the solution of PVA in water was added dropwise to the resulting mixture. After continuing the reaction for 7 h, the product was collected by drying in vacuo over P$_4$O$_{10}$ for 20 h. A series of PDMAEMA/PVA copolymer materials with different PDMAEMA/PVA weight ratio such as 85:15, 80:20, 75:25, 70:30, and 65:35 were prepared by using the similar procedure, and the corresponding products were labeled as P-85, P-80, P-75, P-70, and P-65, respectively.

2.3. Gas Phase Pulse-Measuring QCM System and Testing Process. In this study, the drop coating procedure was similar to that used in the reported literature.[24] The PDMAEMA/PVA copolymers were dissolved in DMSO to obtain the polymer-DMSO solution (5.0 μg μL^{-1}). The resulting copolymer solution (4 μL) was subsequently added onto one side of the QCM gold electrode by a microsyringe. After the solvent evaporated completely in vacuo, a stable film was deposited on one side of the gold electrode surface.

A homemade gas phase pulse-measuring QCM system consisted of a synthesized polymer-coated QCM sensor, a reaction cell, an oscillator detector, a frequency counter and a computer, as depicted in Scheme 1.[25] A vaporization pad allowed the CWA simulants such as DCP, DCE, and DMMP to be evaporated. Predried pure nitrogen was used as carrier gas and the flow rate was controlled by using an Alicat mass flow meter at 360 ± 2 mL min^{-1}. All the vapor tests were performed at room temperature. After the simulants (5 μL) were injected into this measuring system, the frequency (f) of a quartz crystal resonator was recorded through the frequency counter and frequency shifts (Δf) were observed from the frequency−time curve. A bigger frequency shift (Δf) would imply a stronger interaction between the simulant and the PDMAEMA/PVA membrane.

Scheme 1. Gas Phase Pulse-Measuring QCM System
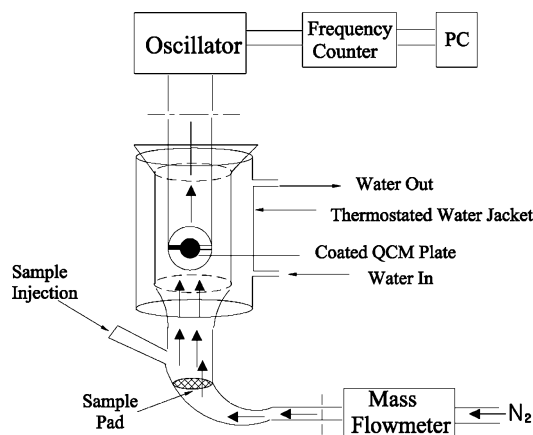
2.4. Luminescent Spectra Studies. Under the excitation of 372 nm, luminescent spectrum of PDMAEMA/PVA copolymers in DMSO solution (1.0 mL, 1.0 g L^{-1}) was measured in quartz cell (1.0 cm) at room temperature. Then, DCP in DMSO solution (20 μL, 2% V/V) was added into this cell. After mixing them for 5 min, luminescent spectra of the resulting mixture had been recorded under the same experimental condition. Addition of DCP solution (20 mL each time) had been repeated for five times to the same cell, and luminescence was recorded after each addition. Finally, the potential reaction mechanism between PDMAEMA/PVA copolymers and DCP had been investigated by the change of emission intensity in luminescent spectra of the resulting mixture.

3. RESULTS AND DISCUSSION

3.1. IR Spectra. As shown in Figure S1 in the Supporting Information, the bands of C=O (1732 cm^{-1}) and C−O−C (1155 cm^{-1}) were characteristic bands from PDMAEMA. In addition, the strong and broad absorption bands observed at 3418 cm^{-1} were ascribed to the ν(O−H) vibration of PVA, which was a clear indication that PVA had been mixed into PDMAEMA during the emulsion polymerization.

3.2. Degradation of DCP on the PDMAEMA/PVA Membranes. In this work, degradation of DCP had been investigated through the PDMAEMA/PVA copolymers-coated QCM sensors (PC-QCM). In addition, the effect of the content of PDMAEMA in these copolymers on degradation of DCP would be discussed in detail. The frequency (f) of quartz crystal-time curves were shown in Figure S2 in the Supporting Information. According to the Sauerbrey equation (eq 1),[6,26] the mass change (Δm) of the PDMAEMA/PVA films could be calculated by frequency shifts (Δf) of quartz crystal resonators, which was explained by chemisorption of DCP in the PDMAEMA/PVA membranes.

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\rho_q \mu_q}}$$

(1)

where f_0 is the measured resonant frequency of quartz crystal, A is the electrode area (0.1963 cm^2 in this work), μ_q and ρ_q are the shear modulus (2.95 × 10^{11} g cm^{-1} s^{-2}) and the density (2.65 g cm^{-3}), respectively.

Moreover, in order to further investigate the degradability of sarin simulants on the PDMAEMA/PVA membranes, chemisorption efficiency (ω) of the PDMAEMA/PVA copolymers in

these assembled PC-QCMs was defined (eq 2) according to the literature.[27]

$$\omega = \frac{\Delta m}{M} \times 100\% \tag{2}$$

where Δm is regarded as the mass of chemisorption for DCP in the copolymer membrane and M is the total mass of the PDMAEMA/PVA film coated on the gold electrode (20 μg in this work).

The results from QCM measurements were listed in Table 1. For PVA film, the frequency shift (Δf) of the quartz crystal

Table 1. Frequency Shifts (Δf), Mass Change (Δm), and Chemisorption Efficiency (ω) for Various PDMAEMA/PVA Membranes Obtained from the QCM Measurements

samples	f_0 (Hz)	Δf (Hz)	Δm (μg)	ω (%)
noncoated sensor	7979016	−9	0.0123	0.06
PVA-coated sensor	7964587	−13	0.0178	0.09
P-65-coated sensor	7973541	−198	0.2701	1.35
P-70-coated sensor	7973577	−223	0.3042	1.52
P-75-coated sensor	7971544	−265	0.3617	1.81
P-80-coated sensor	7974911	−489	0.6668	3.33
P-85-coated sensor	7973688	−671	0.9153	4.58
PDMAEMA -coated sensor	7972548	−1563	2.0958	10.48

resonator was −13 Hz, and the mass change (Δm) was only 0.0178 μg, which was close to that for the noncoated sensor (Δf = −9 Hz). For other sensors coated with different PDMAEMA/PVA copolymers, Δf, Δm, and chemisorption efficiency (ω) increased rapidly with the increasing PDMAE-MA in the copolymers. For PDMAEMA-coated QCM sensor, both the response (1536 Hz) and corresponding ω (10.48%) reached a maximum in the whole series. Thus, these results indicated that pure PDEMAEMA membrane showed the best degradability to DCP among the PDMAEMA/PVA materials. In other words, the active compound to degrade DCP was PDEMAEMA rather than PVA in the PDMAEMA/PVA copolymers. In addition, the PDMAEMA/PVA copolymers with various content of PDMAEMA displayed different degradability in this work. The higher the content of PDMAEMA, the better degradability for the corresponding copolymer film to DCP would be observed.

The ideal protective materials should have excellent degradability to chemical warfare agents, high barrier abilities for toxic compounds, as well as good water vapor transmission (WVT),[6] etc. Water vapor transmission for these PDMAEMA/PVA films with different PDMAEMA content had been investigated in our previous work.[23] The effect of PDMAEMA content for the degradability as well as water vapor permeability of the corresponding PDMAEMA/PVA films was shown in Figure 1. Obviously, the PDMAEMA/PVA films containing more PDMAEMA such as P-100 and P-85 materials displayed the better degradability to DCP, whereas they had smaller WVT rate due to low PVA content. The hybrids film with 75 and 70 wt % of PDMAEMA content had good WVT rate but the degradability to DCP was too weak. The best candidate for chemical warfare protective materials was the PDMAEMA/PVA hybrids with 80 wt % PDMAEMA content (P-80) in this work. It possessed both good degradability to DCP and high WVT rate in the whole series.

3.3. Interaction between P-80 Membrane and the CWA Simulants. Because P-80 had shown both the good
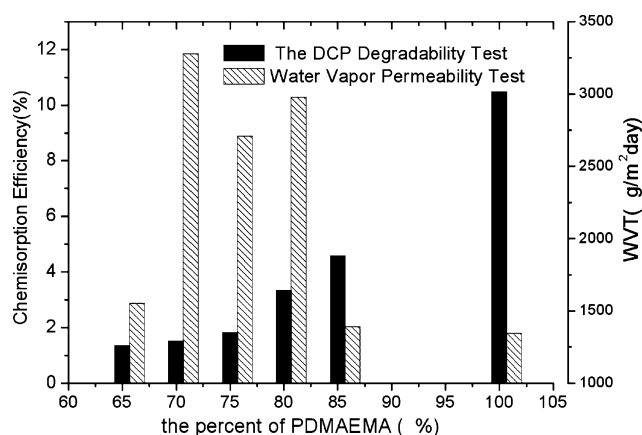

Figure 1. Results of the DCP degradability test and water vapor permeability test for a series of PDMAEMA/PVA films with different DMAEMA content.

degradability to DCP and high WVT rate, it was selected for further investigation of other CWA simulants (DMMP and DCE). As was well-known, DMMP was also regarded as the simulant of sarin and DCE was the simulant of sulfur mustard due to the similar molecular structure and low reactivity. Experiments had been done under conditions similar to DCP and results were shown in Figure 2. It was obvious that three
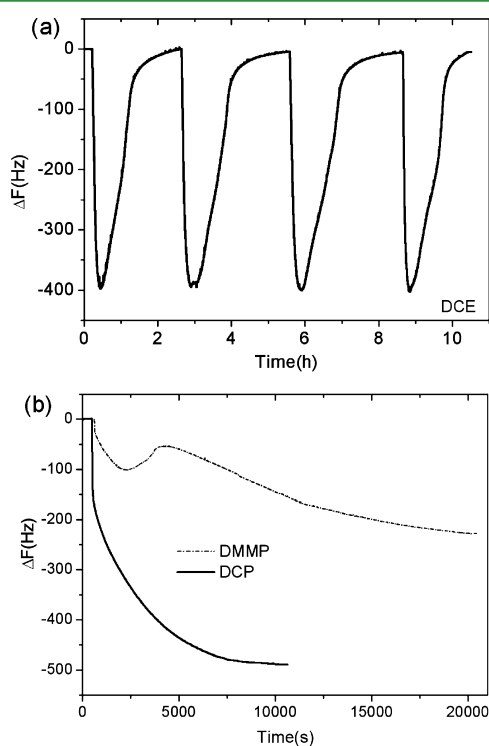

Figure 2. Real-time response curves of polymer coated-QCM sensors with three simulants: (a) DCE, (b) DMMP and DCP.

simulants (DCP, DMMP and DCE) had different interactions with the P-80-coated QCM sensors. From the curves, P-80 only had physical adsorption to DCE, and embodying highly chemisorption with DCP, while giving both physisorption and chemisorption at a certain level to DMMP.

In the real-time response curve of the P-80-coated QCM sensor interacting with DCE (Figure 2a), the frequency of

quartz crystal in the QCM sensor declined quickly with the injection of DCE (5 μL) into the chamber and the frequency change value (Δf) reached the minimum (-395 Hz) after 600 s, which might be explained by the easy absorption of DCE vapor on P-80. Stable nitrogen flow had been kept and the frequency gradually increased until it returned to the baseline level after about 2.3 h. This could be explained by the gradual desorption of DCE vapor with continuous N_2 flow. This experiment was repeated several times under the same conditions and similar results were obtained as shown in Figure 2a. Thus, the complete adsorption−desorption for DCE molecules on the surface of P-80 indicated that only physisorption for DCE molecules occurred on the surface of PC-QCM sensor.

Similar studies for DMMP vapor had been carried out under the same conditions and significantly different response curve for the PC-QCM sensor to DMMP vapor was illustrated in Figure 2b. First, the frequency significantly went down by -103 Hz within 1560 s after DMMP (5 μL) was injected into the chamber. Then, the frequency increased gradually with the measurement time prolonging and the Δf value was back to -54 Hz at 3560 s. However, to be surprised, the frequency of quartz crystal decreased again after 3560s instead of increasing. Finally, the frequency shift (Δf) was up to -228 Hz after injecting DMMP vapor 19616 s from the beginning. These results indicated that there were typical physisorption as well as chemisorption during the interactions between DMMP molecules and P-80 materials. Before 3560s, the resonance frequency of quartz crystal showed a similar change to that of DCE, which might be ascribed to the physisorption of P-80. However, during the period (3650s-19616s), chemisorption of DMMP onto P-80 became predominant, because the chemical absorption rate of P-80 to DMMP vapor was greater than the desorption rate of DMMP vapor upon flush of nitrogen gas. Finally, the chemical absorption and desorption rate slowly reached an equillibrium as the chemisorption reaction sites in P-80 were occupied.

For DCP, remarkably different experimental phenomena had been observed. As shown in Figure 2b, the frequency quickly decreased by about 160 Hz after injecting DCP sample for 80 s. Then, rate of frequency change became smaller because the adsorption sites were gradually occupied by DCP molecules. Finally, the frequency of quartz crystal remained in a stable state starting from 9960 s and the maximum response was 486 Hz. These results indicated that DCP molecules had been steadily combined with P-80 through the strong chemisorption after they were injected into the chamber and hardly desorbed despite the stable flowing of nitrogen gas. Thus, the frequency of quartz crystal had been falling until the equilibrium state.

When comparing with the three kinds of real-time response frequency curves (Figure 2), three different interaction models were observed, namely adsorption−desorption model, adsorption−desorption−chemisoportion model and pure chemisoportion model corresponding to DCE, DMMP and DCP vapor, respectively. DCP, being a chloro-substituted organic phosphate, was more reactive than DMMP, a methyl-substituted organic phosphate. This structure difference could explain the higher chemisorptions of DCP on P-80.[28] Thus, these PC-QCM sensors coated with the reactive polymers would have potential applications in discriminating the interaction mechanisms for various chemical warfare agents.

3.4. Luminescent Studies for the PDMAEMA/PVA Copolymers.
As depicted in Figure S3 in the Supporting

Information, P-80 copolymer showed characteristic blue emission at the excited wavelength of 365 nm. The blue fluorescence came from the tertiary amino groups in the PDMAEMA/PVA copolymers, similar to the reported visible fluorescence from some hyperbranched polymers and dendrimers containing tertiary amino groups.[29,30] After adding excess DCE molecules on the surface of this copolymer, its luminescence remained unchanged. However, the luminescence of P-80 copolymer was quenching with the addition of DCP and completely disappeared after reacting with excess DCP molecules. Such interesting phenomena indicated that the interactions between DCE molecules and P-80 did not affect the structure of the polymer. In contrast, the interactions between DCP and P-80 might lead to the structure change of the fluorescence active group in P-80 − the tertiary amino group. The fluorescent studies further confirmed that the interaction between the PDMAEMA/PVA copolymers and DCP molecules was a typical chemisoportion consistent with the previous QCM studies.

Moreover, the fluorescent behaviors for the mixtures of P-80 copolymer and DCP had been further investigated in detail at room temperature, as illustrated in Figure 3a. Obviously, the
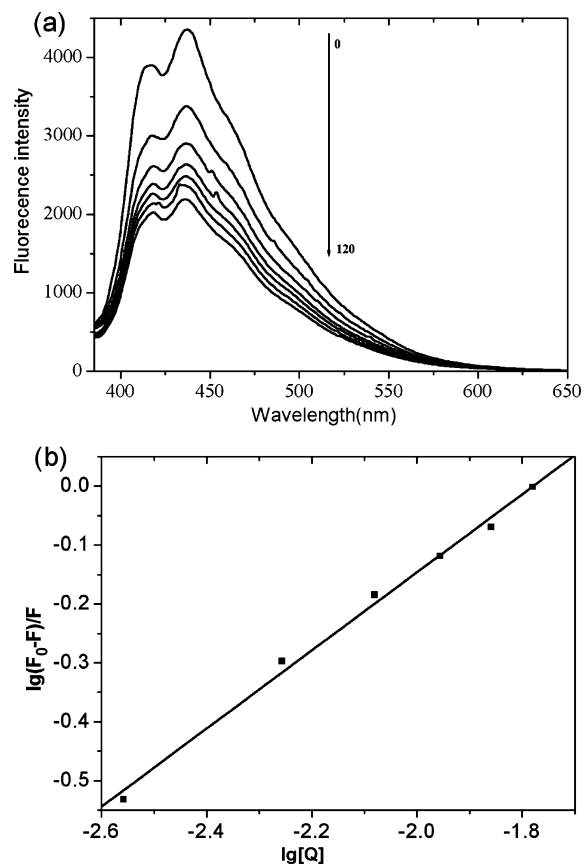

Figure 3. a) Fluorescence spectra of P-80 copolymer with DCP in DMSO solution excited at 372 nm, together with (b) the calibration curve for the emission intensity changes with volume concentration of DCP in log−log plot. The corresponding volume of DCP were 0, 20, 40, 60, 80, 100, and 120 μL from top to down with P-80 copolymer (1.0 mL, 1.0 g L^{-1}), respectively.

DMSO solution of P-80 copolymer still displayed visible blue

emission, and its fluorescence spectrum presented a broad band

in the range of 400−600 nm with maximum emission at 438

nm when excited at 372 nm. When 20 μL DCP solution (in DMSO, 2% V/V) was added to the P-80 solution, the spectrum of the resulting mixture (λ_{max} = 438 nm) remained unchanged, except the fluorescent intensities remarkably weakened. Subsequently the addition of DCP (20 μL each) for five times resulted in similar phenomena and the fluorescence intensity gradually weakened with the increase in the total volume of DCP solution (from 0 to 120 μL) (Figure 3a).

Fluorescence quenching could usually be categorized into dynamic quenching and static quencher according to the quenching mechanisms. The dynamic quenching was caused by the collision between fluorescent molecules and quenchers, whereas static quenching was due to the production of nonfluorescence complexes through the reaction of fluorescent molecules and quenchers. On the basis of the current experiments results, it was inferred that P-80 copolymer fluorescence quenching with DCP molecules was mainly due to static quenching. Thus, the binding constant K_a of DCP with P-80 copolymer could be elicited from the static quenching equation,[31] as shown in eq 3.

$$\lg \frac{F_0 - F}{F} = \lg K_a + n\lg[Q] \tag{3}$$

where n is the number of the binding sites, $[Q]$ is the concentration of DCP (V/V) in the quartz colorimetric dish, F_0 is the fluorescence intensity of P-80 copolymer, and F is the fluorescence intensity after interaction with DCP. K_a can be deduced from the intercept of the linear regressions.

As illustrated in Figure 3b, the fluorescence intensities of DCP-P-80 copolymer nicely fitted the static quenching equation, in which the fitting correlation coefficient was 0.9952. These results suggested that PDMAEMA/PVA copolymers fluorescence quenching with DCP molecules was due to static quenching and the reactions between PDMAEMA polymers with DCP molecules resulted in new nonfluorescent substances.

3.5. ¹H NMR Studies. According to the QCM studies mentioned above and previous publications,[23,32] it is clearly demonstrated that PDEMAEMA have good degradability to DCP rather than PVA in the PDMAEMA/PVA copolymers. Thus, ¹H NMR spectra for pure DMAEMA and DCP were measured in DMSO-d⁶ solution under room temperature, as depicted in Figure 4. In addition, ¹H NMR spectrum for the mixture of DMAEMA and DCP (after reacting for 2 h) was also recorded under the similar conditions.

In Figure 4(1), the signals at 5.657 and 5.995 ppm corresponded to the methylene protons of DMAEMA, and two groups of peaks were observed at 2.493 and 4.147 ppm, corresponding to two −CH₂− protons of DMAEMA. In addition, the signals at 1.856 and 2.156 ppm were ascribed to chemical shifts of protons from one −CH₃ and two N−CH₃ groups, respectively. For DCP, the signals of the ethyl protons appeared at 1.145 and 3.862 ppm, respectively.

However, in the ¹H NMR spectrum for the mixture of DMAEMA and DCP, the signal at 2.156 ppm, which was ascribed to the N−CH₃ protons of DMAEMA, shifted to downfield direction and was observed at 2.763 ppm. The other peaks for DMAEMA did not change and still appeared at the similar position. The signals of ethyl protons of DCP were also observed at the similar position, which might be explained that and the reaction between DCP and DMAEMA did not have obvious effect on ethyl groups and the chemical environment still remained. Thus, the NMR studies further indicated that the
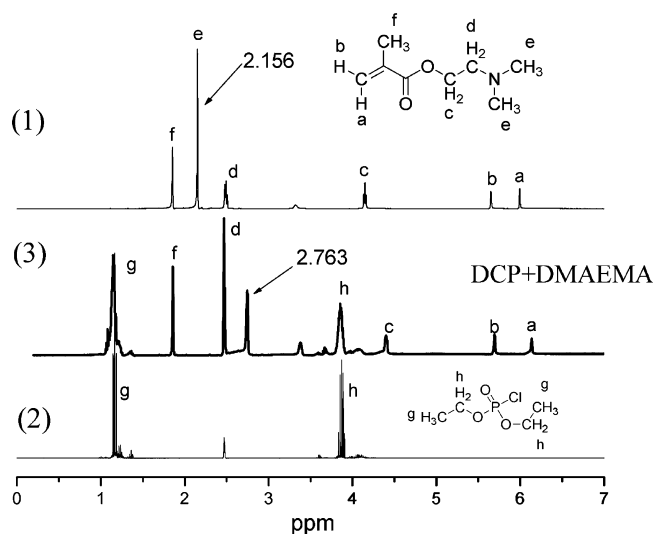

Figure 4. ¹H NMR spectra of DMAEMA (1), DCP (2), and the mixture of DMAEMA and DCP (3) measured in DMSO-d_6 solution.

N−CH₃ group in DMAEMA has played the crucial role in the degradating reaction with DCP, which was consistent with the fluorescent results.

4. CONCLUSIONS

In summary, we have successfully constructed a new series of polymer-coated QCM sensors (PC-QCMs) through coating PDMAEMA/PVA copolymers on the surface of QCM Au electrodes. These PC-QCMs have been applied to investigate the interactions between the copolymers and chemical warfare agent simulants (DCP, DCE, and DMMP). Most interestingly, different response models were observed for three simulants. The interactions between PDMAEMA/PVA copolymers with sarin simulants (DCP and DMMP) are mainly attributed to the chemisorption, whereas that with DCE is due to the physisorption. In addition, fluorescent spectroscopy has been used to investigate the interactions between the PDMAEMA/PVA copolymers and the simulant DCP. The quenching of fluorescence is mainly ascribed to static quenching resulting from formation of new nonfluorescent substances by the reactions between PDMAEMA polymers and DCP molecules. The strong interaction between the copolymer and DCP is consistent with the QCM results. To the best of our knowledge, this PC-QCM approach has been applied to investigate the degradation of chemical warfare agent simulants on reactive polymeric materials for the first time. To conclude, the PDMAEMA/PVA copolymers exhibit good degradability to DCP as well as high water moisture vapor permeability, and they may be a class of potential protective materials toward chemical warfare agents.

■ ASSOCIATED CONTENT

ⓈSupporting Information

FT-IR spectra of PVA, PDMAEMA, and PDMAEMA/PVA-80 copolymer; QCM spectra for the interactions between DCP and PDMAEMA/PVA copolymers; and the photographs of P-80, P-80 with DCE, and P-80 with DCP excited by a UV lamp. The material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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