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Effect of the Molecular Size of Analytes on Polydiacetylene Chromism

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The pH chromism of polydiacetylenes (PDAs) is examined with respect to the molecular size and acidity of acid analytes, along with the alkyl spacer length of primary-amine-functionalized diacetylene (DA) lipids. pH turns out to be an important parameter to charge amine headgroups of PDA but a change in pH does not necessarily result in a PDA color change. The molecular size of acid analytes is identified as another factor that can produce a configurational change in PDA amine headgroups, followed by perturbation of the ene–yne conjugated backbone. In addition, the length of a flexible alkyl spacer between the amine headgroup and the amide group of the diacetylene lipids is found to strongly affect the degree of PDA chromatic transition. The longer alkyl spacer shows a smaller chromatic transition from blue to red phase. The alkyl spacer seems to provide a certain degree of freedom to the amine headgroup, thus decreasing the transfer of headgroup steric effects to the PDA backbone. These correlations found for PDA chromism are applied to the development of a system that colorimetrically detects diethyl phosphate (DEP), a degraded nerve agent simulant. PDA liposomes show a selective chromatic transition upon binding with DEP compared to other acid analytes.

1. Introduction

The molecular design of diacetylenes (DAs) has been of great interest since the mechanism of topochemical polymerization was uncovered.[1] To satisfy the requirements for their polymerization,[2] the interactions between adjacent functional groups on DA molecules have been scrutinized. Aromatic interactions, hydrogen bonding, and hydrophobic interactions were found to be effective for the self-assembly and polymerization of DA molecules when they are properly combined and tailored.[3–7] In addition, external stimuli such as heat,[8] pH,[9] mechanical stress,[10] or ligand-receptor binding[11] have been found to induce a polydiacetylene (PDA) color change and various sensor applications have been proposed based on these chromisms.[12–23]

Salt formation or electrostatic interactions have not been only employed in the assembly of DA molecules, but PDA chromism based on pH changes has also been studied. More specifically, carboxylic acid functionalized PDAs have been widely investigated with regard to pH change. A study of 10,12-pentacosadiynoic acid (PCDA) monolayers suggests that the ionization of the carboxylic acid group at high pH causes a disordered configuration due to salt formation with counterions. This change in configuration induces the optical transition from blue phase to red phase.[24] When the pH is lowered back towards the original level, bathochromic shifts are observed in absorption spectra of PDAs, where yellow phase transitions to red phase[25] or red phase to blue phase.[26–30] These chromatic transitions are attributed to a conformational change that results in an increase in the degree of conjugation of the PDA backbone.[9] It seems to have been consistently shown that the replacement of hydrogens bonds with electrostatic interactions may cause a significant change in the configuration of DA or PDA headgroups, as well as a change in the electronic state of PDA's conjugated backbone. pH change, which can be a driving force for electrostatic interaction, is one of stimuli known to cause color change from blue phase to red phase, as well as fluorescent emission in PDA. The intensity of this interaction is controlled by the pH level and is believed to be a direct result of the degree of the conformational change in the PDA conjugated backbone. Accordingly, the acidity or basicity represented by pH level has been solely correlated with these PDA chromatic transitions.

Furthermore, an interesting result was reported about basic-headgroup-functionalized DA, which provides more detailed information on the configuration of DA headgroups due to salt formation.[31] The polymerization of these initially unpolymerizable monomers functionalized with hydrazide was achieved by the addition of HCl. This result was explained by a change in the distance between adjacent headgroups. According to computational studies, hydrogen bonding between amine headgroups made the distance between DA units (3 Å) too short for polymerization. HCl salt formation on amine functional groups resulted in a larger distance between molecules (4.9 Å), which seems to be more favorable for topochemical polymerization.

In this contribution, it is demonstrated that a certain pH level is necessary to create salt formation through an acid–base reaction on the PDA headgroup. However, it is not the only criteria to induce

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the chromatic transition of PDA. Considering the space occupied by the counterion, the chromatic transition of PDA liposomes was investigated in terms of the molecular weight and the pH level of acid analytes. Molecular weight was adopted in convenience to produce appreciable data for the effect of molecular size. It was found that a strong correlation exists between the extent of PDA chromatic transition and the molecular size of acid analytes. When the acidity of analytes is strong enough to pull counterions into the surface of the amine headgroups, it is suggested that the molecular size of acid analytes causes steric effects and induces the chromatic transition of amine-functionalized PDAs. The size-selectivity of PDA chromism was applied to distinguish diethyl phosphate (DEP) from general acids. This could be used in the detection of nontoxic degraded acids from the hydrolysis of toxic organophosphorus agents (Fig. 1). In addition, it was shown that flexible alkyl spacers affect this chromism by decreasing the extent of PDA chromatic transition as the length of the alkyl spacers increases.

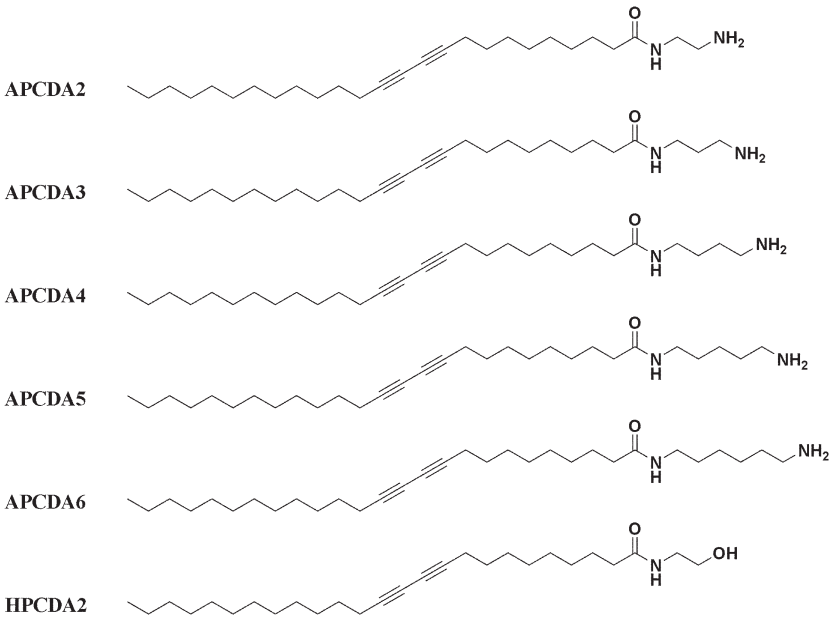

Figure 2. DA monomers of APCDA*n* ($n = 2 \sim 6$) and HPCDA2.

2. Results and Discussion

The primary-amine-functionalized DAs of *N*-(*n*-aminoalkyl)-10,12-pentacosadiynamide (APCDA*n*, $n = 2 \sim 6$) and the hydroxy-functionalized DA of *N*-(2-hydroxyethyl)-10,12-pentacosadiynamide (HPCDA2) were synthesized and their chemical structures are shown in Figure 2. The length of the alkyl spacer between amine and amide groups of APCDA*n* was varied from two to six methylene groups.

2.1. Effects of Molecular Size and pH on Polydiacetylene Chromism

In order to study the effects of molecular size and pH of acid analytes on PDA chromism, a series of alkanoic acids were chosen

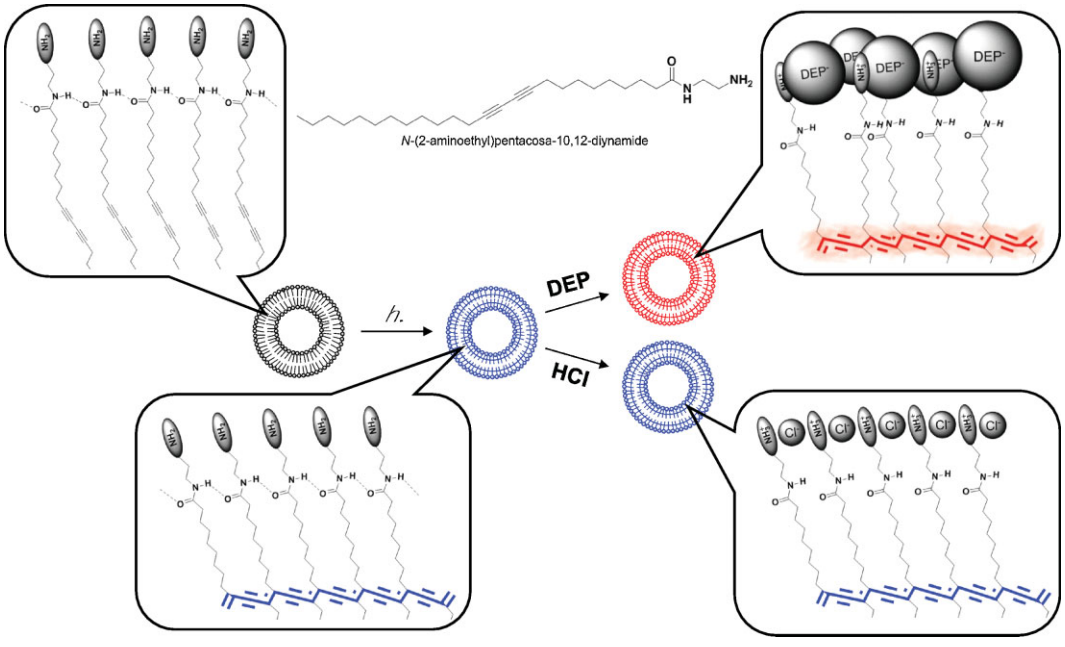

Figure 1. Schematic illustration of PDA's selective chromatic transition dependent on the molecular size of acid analytes.

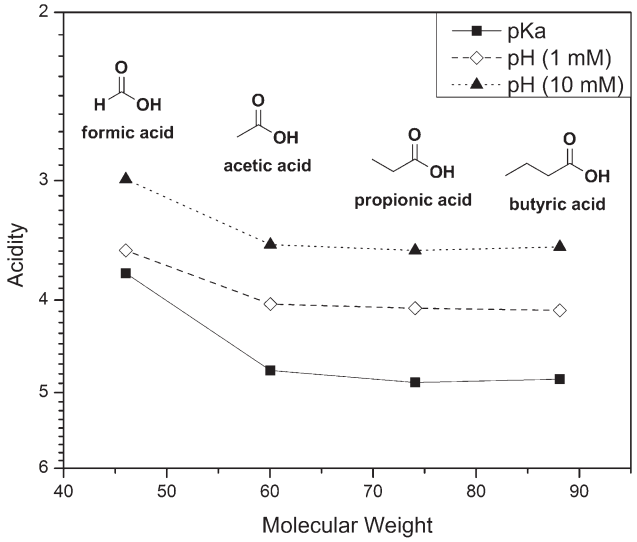

Figure 3. Acidity of alkanoic acids with respect to molecular weight.

and PDA liposomes were prepared with APCDA2. Alkanoic acid is the simplest carboxylic acid (R—COOH, R = H or alkyl group) having moderate acidity, as most carboxylic acids are generally weak acids. The acidity of short-chain alkanoic acids tends to decrease as the number of methylene group increases, as shown in Figure 3. Formic acid (MW 46.03, pKa 3.75) shows the strongest acidity among these acids and the acidity decreases in the order of acetic acid (MW 60.05, pKa 4.76), propionic acid (MW 74.08, pKa 4.87), and butyric acid (MW 88.11, pKa 4.83).[32] This tendency gradually lessens and the acidity of butyric acid is almost similar to that of propionic acid. These acids were added to the APCDA2 liposome solution in such a way that the final concentration of the liposome solution was 0.05 mM and that of the acids was either 0.1, 1, or 10 mM. The absorption spectra of APCDA2 liposome solutions were monitored upon the addition of the acids. The extent of the chromatic transition from blue to red phase was quantified by colorimetric responses (CRs) as previously defined.[33]

As shown in Figure 4, the addition of 0.1 mM formic acid in APCDA2 liposome solution hardly induced the transition from blue to red phase. Although raising the concentration of formic acid to 1 and 10 mM increased the extent of the transition, these transitions were still not considerable enough to distinguish the color transition by the naked eye. The additions of other acids at 10 mM concentrations induced successively increasing transitions. A remarkable color transition from blue to red phase was observed with a CR over 50% when butyric acid was added to the APCDA2 liposome solution. On the other hand, 0.1 and 1 mM concentrations of those acids induced only slight transitions.

Individually, each alkanoic acid showed APCDA2 color transitions that were dependent on acid concentration or pH level. As the pH level of each acid was lowered, the CR values of the APCDA2 liposome solution increased. To the contrary, the transitions induced by the addition of 10 mM alkanoic acids showed a strong dependency on molecular weight rather than pH level. These data suggest that the molecular size effect is dominant for pH chromism in PDA, where the strength of acidity is still a necessary factor since it is the driving force for salt formation. At lower acidity of ca. pH > 4, alkanoic acids did not induce any noticeable chromatic transition, probably because their electrostatic interactions with the amines were not strong enough to cause a significant change in the configuration of the APCDA2 headgroup. Note that the hydrophobicity of the acids increases along with the molecular size. However, because the acids are completely soluble in water and do not form any assembly the hydrophobicity is not likely responsible for the trend of the PDA chromism.

2.2. Molecular-Size-Dependent Detection of DEP

Simple, low-cost, and reliable detection of nerve agents is a great challenge owing to the elusive reactivity of toxic organophosphorus compounds.[34–38] Although great efforts have been made to implement their detection,[39–44] conventional analytical methods such as gas/liquid chromatography, mass spectroscopy, and NMR spectroscopy are still considered as the most assuring techniques for their accurate identification.[45,46] It is known that toxic organophosphorus compounds are degraded to nontoxic phosphonic acids by hydrolysis [45–49] and the detection of these acids has been recently interesting as an indirect alternative to infer any use of their toxic parent compounds.[50–53] The molecular size effect found for the chromism of the APCDA2 liposome was applied to distinguish DEP from general strong acids frequently used in the laboratory. DEP was obtained by the hydrolysis of diethyl chlorophosphate (DCP), one of nerve agent simulants, as shown in Figure 5. Since HF and HCl among other acids may come not only from the degradation of those agents or simulants but also from other routes, the distinction between these acids and DEP provides an advanced selectivity in this field.

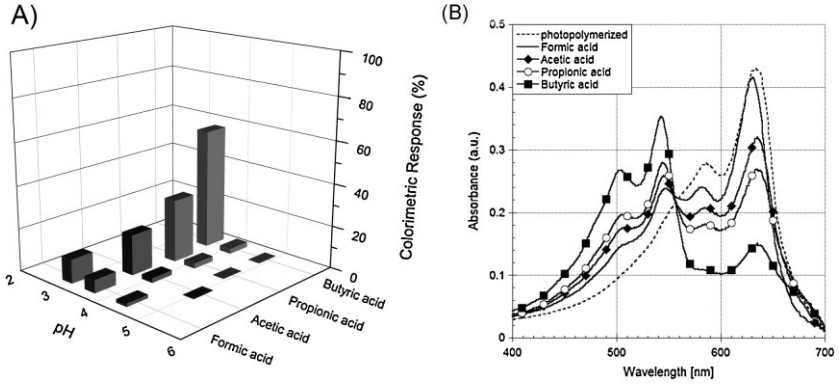

Figure 4. APCDA2 liposome chromatic transitions induced by alkanoic acids. A) CRs on additions of 0.1, 1, and 10 mM acids with respect to pH. B) Absorption spectra on additions of acids (10 mM).

Absorption and photoluminescence (PL) spectra of APCDA2 liposomes were measured following each addition of acid and the CRs were calculated, as shown in Figure 6. The acidities of 0.1 mM solutions of these acids were not strong

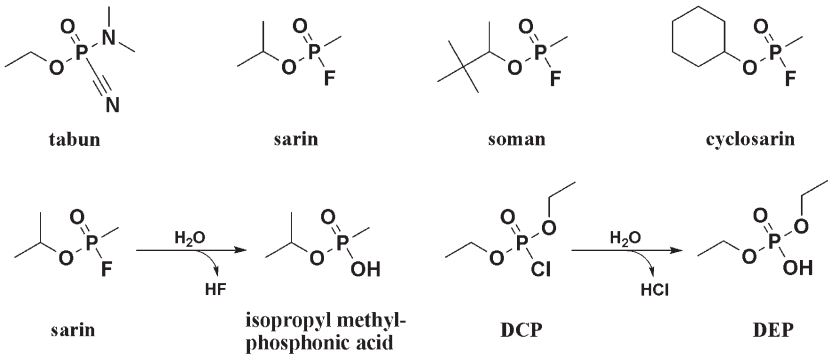

Figure 5. G-type nerve agents with DCP simulant and their hydrolytic degradation.

enough to induce chromatic transitions comparable to 0.1 or 1 mM solutions of alkanoic acids. The 1 mM solutions of these acids have a narrow acidity range of pH 2.8 ~ 3.4, which is strong enough to induce a transition. The molecular weights of the acids vary from 20.01 (HF) to 154.10 (DEP). The degree of the chromatic transition of the APCDA2 liposomes again showed a strong correlation with the molecular weight of the acid analytes, as observed in the study of alkanoic acids. The addition of DEP, which has the largest molecular weight among the acids and is the second weakest acid to HF in this study, induced almost a full transition to red phase (CR 90.0%, Fig. 6B) with strong fluorescent emission (Fig. 6D). The addition of HNO_3 (MW 63.01, CR 9.0%), H_3PO_4 (MW 98.00, CR 12.5%), and H_2SO_4 (MW 98.08, CR 21.7%) induced small transitions to the red phase. The stronger acidity of H_2SO_4 may have caused a larger chromatic transition than that of H_3PO_4 and induced a slight color change toward purple to the naked eye.

Intriguingly, diatomic acids induced unusual chromatic transitions in APCDA2 liposomes. As shown in Figure 6A, the addition of HF, HCl, and HBr induced bathochromic shifts as well as considerable hyperchromic effects in the absorption spectra of APCDA2 liposomes. Instead of chromatic transitions from blue to red phase, the additions of HF, HCl, and HBr red-shifted the absorption maxima of the APCDA2 liposomes by 11, 15, and 10 nm with intensity increases of 30%,

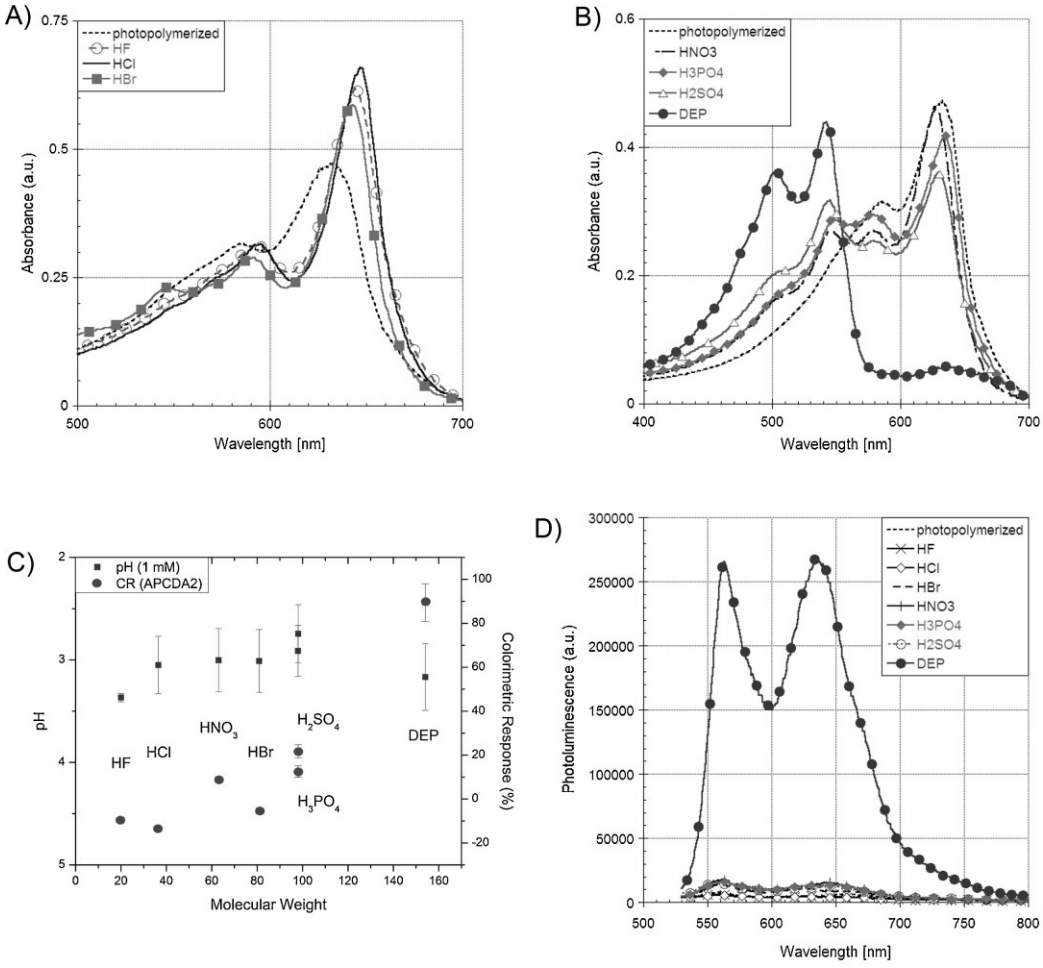

Figure 6. APCDA2 liposomes chromatic transitions induced by general acids and DEP (1 mM). A) Absorption spectra on additions of diatomic acids. B) Absorption spectra on additions of multiatomic acids. C) CRs with respect to molecular weight and pH. D) PL spectra (excitation: 503 nm).

38%, and 24%, respectively. The negative CR numbers of HF (−8.8%), HCl (−13%), and HBr (−6.3%) added to APCDA2 liposomes came from a considerable increase of the blue phase. The addition of HBr to APCDA2 liposomes also induced a slight transition to the red phase, while HF and HCl did not develop any red phase. Similar hyperchromic effects with bathochromic shifts of absorption spectra have been previously reported as the result of increased conjugation in the polymer backbone.[54–57] These unusual results by diatomic acids indicate that intact APCDA2 liposome headgroups may not form the most favorable spatial arrangement for the conjugation of PDA backbone. Since the distance or angle between adjacent DAs usually changes during topochemical polymerization,[58,59] whereas interactions between headgroups are retained, these possibly discordant behaviors between PDA backbone and headgroup may cause an unrelaxed conformation in the PDA backbone.[60] In addition, it was previously shown that the hydrogen bonds between amine headgroups do not make an optimal configuration for DA assembly and topochemical polymerization, while HCl salt on amine headgroups was found to provide a polymerizable configuration. Therefore, our data also imply that the salt formation on amine headgroups by small-molecular-weight diatomic acids replaces the hydrogen bonds by the electrostatic interaction and rearranges the configuration of the amine headgroups, which improves the conjugation in the PDA backbone. Furthermore, the rearrangement of the charged headgroup by HCl seems to increase the degree of conjugation more than HF and HBr. This ''salt annealing effect'' by these diatomic acids is indeed similar to the effect of heat annealing on PDA. Thermally pre-annealed DA films show bathochromic shifts with hyperchromic effects through polymerization compared to untreated DA films.[61]

2.3. Effect of Alkyl Spacer on PDA Chromism

APCDA*n*, a series of DA with alkyl spacer length varied from two to six methylene groups, was examined by the addition of general acids and DEP. After photopolymerization, it was interesting to find that liposomes with longer alkyl spacers efficiently developed the blue phase with shorter UV irradiation time (see Supporting Information, Fig. S4). The full development of the blue phase from APCDA2 liposomes took about 90 s of UV irradiation. The irradiation time necessary for a full development of the blue phase decreased to about 60 and 40 s for APCDA3 and APCDA4 liposomes, respectively. Only about 30 s was enough to achieve the full blue phase of APCDA5 and APCDA6 liposomes. Prolonged UV irradiation after formation of the full blue phase continued to develop the vibronic peak of the blue phase but eventually the peak from the red phase became dominant. As mentioned above, the hydrazide-functionalized DA liposomes without any spacer between the amine headgroup and amide group (APCDA0) is not polymerizable. Our data obtained from this study show that the alkyl spacer promotes topochemical reaction.

Acid analytes were added to polymerized APCDA*n* liposome solutions. As shown in Figure 7, it was found again that the sterics created by salt formation at the PDA headgroup induce chromatic transitions that depend on the molecular size of the acid analytes. Furthermore, the degree of discrimination by molecular size, or

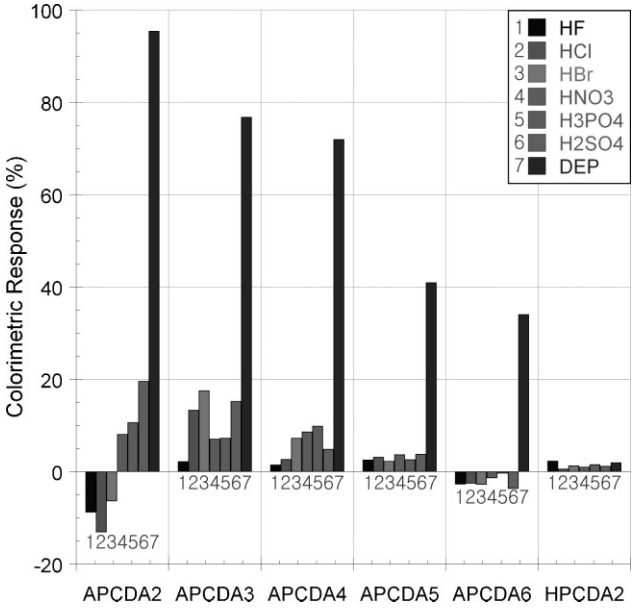

Figure 7. CRs of APCDA*n* and HPCDA2 liposomes on addition of general acids and DEP.

selectivity, decreases as the length of alkyl spacer increases. The liposome solutions with longer alkyl spacers have smaller chromatic transitions from blue to red phase when the same analytes are compared, as previously reported.[25] The CR of APCDA2 liposomes induced by DEP is about 95.5%, whereas that of APCDA6 by DEP is 34%. The control sample, the HPCDA2 liposome solution, did not have any noticeable chromatic transition when any of the acids were added.

According to both studies, the length of alkyl spacer seems to substantially influence the configuration of the self-assembled DA as well as the conformation of PDA's conjugated backbone. The unfavorable effect of hydrogen bonding between amine headgroups decreases after polymerization and the degree of PDA chromatic transition also decreases as the length of alkyl spacer increases. It is inferred that the alkyl spacer may provide flexibility or a degree of freedom, thus, reducing the association between the conditions of the outer headgroup and the inner hydrophobic part or conjugated backbone.

3. Conclusions

In this study, the molecular size and acidity of analytes were correlated with PDA chromism and the effects of different alkyl spacer lengths were investigated. The degree of the chromatic transition of PDA liposomes was shown to be strongly dependent on the molecular size of acid analytes as well as their pH level. Small diatomic acids proved that pH change does not solely induce PDA chromatic transition from blue to red phase. Rather than producing significant chromatic transitions, diatomic acids produced bathochromic and hyperchromic shifts in the absorbance of APCDA2 liposomes as a result of the salt annealing effect. APCDA2 liposomes showed that the degree of chromatic transition is dependent on the molecular size of alkanoic acids.

Hence, we propose that the charge-induced configurational change on the PDA headgroup may result from the combined effects of molecular size and pH level. These findings were applied to the development of PDA liposomes for the detection of DEP, a hydrolyzed nerve agent simulant. DEP, the largest molecule in this study, induced almost full chromatic transition in APCDA2 liposomes. In addition, the variation in alkyl spacer length of DA provided evidence that flexible alkyl spacers may reduce the degree of association between the PDA headgroup and the conjugated backbone.

4. Experimental

Materials and Syntheses: 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals (Powell, OH). All other reagents and solvents were purchased from Sigma-Aldrich and Acros Organics and used as received. Deionized water was used for the synthesis of DAs, DEP, and the preparation of liposomes and diluted solutions of acid analytes. APCDA*n* ($n = 2 \sim 6$) were synthesized based on the synthetic routes of APCDA2 and HPCDA2 reported previously [62] and characterized by NMR and mass spectroscopies.

APCDA3 (*N*-(3-aminopropyl)-10,12-pentacosadiynamide). 94.4% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.26 (br, 1H), 3.36 (dd, $J = 6.2$, 12.4, 2H), 2.80 (t, $J = 6.3$, 2H), 2.23 (t, $J = 6.9$, 4H), 2.15 (t, $J = 7.6$, 2H), 1.68–1.15 (m), 0.87 (t, $J = 6.7$, 3H); MS (ESI): $[M + H]^+$ calcd for $C_{28}H_{50}N_2O$: 431.4001; found: 431 .4005.

APCDA4 (*N*-(4-aminobutyl)-10,12-pentacosadiynamide). 90.1% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.74 (br, 1H), 3.21 (dd, $J = 6.7$, 12.5, 2H), 2.73 (t, $J = 6.6$, 2H), 2.19 (t, $J = 6.9$, 4H), 2.17 (t, $J = 7.6$, 2H), 1.66–1.15 (m), 0.87 (t, $J = 6.7$, 3H); MS (ESI): $[M + H]^+$ calcd for $C_{29}H_{52}N_2O$: 445.4158; found: 445.4169.

APCDA5 (*N*-(5-aminopentyl)-10,12-pentacosadiynamide). 67.6% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.46 (br, 1H), 3.25 (dd, $J = 7.0$, 13.0, 2H), 2.69 (t, $J = 6.7$, 2H), 2.23 (t, $J = 6.9$, 4H), 2.18–2.10 (t, $J = 7.7$, 2H), 1.66–1.16 (m), 0.88 (t, $J = 6.7$, 3H); MS (ESI): $[M + H]^+$ calcd for $C_{30}H_{54}N_2O$: 459.4314; found: 459.4315.

APCDA6 (*N*-(6-aminohexyl)-10,12-pentacosadiynamide). 88.8% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.44 (br, 1H), 3.24 (dd, $J = 7.1$, 13.0, 2H), 2.70 (t, $J = 6.8$, 2H), 2.24 (t, $J = 7.0$, 4H), 2.18–2.10 (m, 2H), 1.66–1.18 (m), 0.88 (t, $J = 6.7$, 3H); MS (ESI): $[M + H]^+$ calcd for $C_{31}H_{56}N_2O$: 473.4471; found: 473.4489.

DEP. To a solution of 10.34 g (59.93 mmol) of DCP in 5 mL of water in an ice bath ($4 \sim 5$ °C) was added dropwise a solution of 4.79 g (119.85 mmol) of NaOH in 45 mL of water. The mixture solution was allowed to stir for 2 h at room temperature and acidified with 10% HCl. The solvent was evaporated in a vacuum. The residue was dissolved in chloroform, dried over $MgSO_4$, and the solvent was removed by rotary evaporator. The resulting compound was purified by silica gel column chromatography eluting with $CHCl_3$/MeOH (8:1) to yield DEP as a colorless oil (7.33 g, 47.56 mmol, 79.3%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.44 (s, 1H), 4.10 (dq, $J = 14.2$, 7.1, 4H), 1.34 (td, $J = 7.1$, 1.0, 6H); ^{31}P NMR (121 MHz, $CDCl_3$, δ): 0.95.

Preparation and Polymerization of Liposome Solution: Each DA dissolved in chloroform was placed in a 50 mL Erlenmeyer flask and the solvent was dried. Deionized water was added to make a 0.1 mM solution of each DA. The mixture solution was heated in a water bath of 90∼95 °C and probe-sonicated for 20 min with a high-intensity ultrasonic processor (750 W–20 kHz, Cole-Parmer). The resulting solution was filtered through a 0.8 μm filter (Millex-AA, Millipore) and stored at 4 °C for 2 h followed by warming up to room temperature for an additional 2 h prior to photopolymerization. DA liposome solution (2 mL) was put in a quartz cuvette and polymerized by 254 nm light from a hand-held UV lamp (UVGL-25, UVP). UV irradiation was performed for 10 s repeatedly until the excitonic peak of the blue phase did not develop noticeably by the naked eye. The development of the blue phase of the DA liposome solution was monitored by a UV-Vis spectrophotometer after every UV irradiation.

Addition of Acid Analytes and pH Measurement: Each acid (2 mL, 2 mM) was added to 2 mL of PDA liposome solution (0.1 mM) for final concentrations of 1 and 0.05 mM. pH measurement was carried out using a SA520 pH meter (Orion Research Inc.) after the calibration of the pH meter by pH buffer solutions of red (pH 4), yellow (pH 7), and blue (pH 10). Each acid (2 mM) was diluted to 1 mM by adding deionized water and the pH was recorded. The chromatic transitions by the addition of acids were observed by UV-Vis and PL measurements at 30 s, 1 min, and 10 min after the acid addition.

UV-Vis and PL Measurement: UV-Vis absorption spectra were obtained on a Cary 50 UV-Vis spectrophotometer (Varian Inc.) and PL spectra were recorded on a PTI QuantaMaster fluorometer (Photon Technology International), using a quartz cuvette with a 1 cm optical path length.

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