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Formation of Cyclic and Polymeric Structures from Zwitterions

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Covalent linkages that connect atoms are fundamental interactions that produce molecules. The formation and cleavage of covalent bonds by external stimuli can control the states of molecules, such as monomers, oligomers, and polymers. Based on this concept, dynamic covalent polymers have been fabricated by using various exchangeable-bonding strategies, such as those that have been seen in the Diels–Alder reaction and in disulfides.[1,2] A potential strategy for constructing covalent linkages is the nucleophilic attack of an anionic site at a cationic site; in this case, an equilibrium between a covalent bond and an ion-pair state would be observed. Of various cationic units, a trityl cation is a suitable motif that should undergo a nucleophilic attack by anionic species after appropriate modifications of the substituents.[3] In contrast, the triazatriangulenium (TATA) cation[4] (an analog of the trityl cation) prefers a planar structure, which prevents the facile formation of covalent linkages with anionic sites.[5] Therefore, zwitterionic species consisting of a fairly flexible trityl cation and an anionic unit would form covalent polymers depending on conditions.

According to a literature procedure, trityl–phenol cationic species **1a**$^+$, **2a**$^+$, and **3a**$^+$ were prepared as $\mathrm{BF_4}^-$ salts in 20, 19, and 23 % yield, respectively, by the Suzuki coupling reaction of iodo-substituted trityl derivatives with hydroxyphenylboronic acids followed by treatment with $\mathrm{HBF_4}$ (Figure 1 a).[6] Cationic monomer salts $\mathbf{1a}^+\cdot\mathrm{BF_4}^-$, $\mathbf{2a}^+\cdot\mathrm{BF_4}^-$, and $\mathbf{3a}^+\cdot\mathrm{BF_4}^-$ can be considered as precursors of the expected zwitterions **1b**, **2b**, and **3b**, respectively. Introduction of electron-donating dimethylamino moieties to the trityl aryl rings, as was observed in malachite green, is necessary to obtain stable cationic sites that can be attacked nucleophilically by anionic species under the appropriate conditions.[4,7] A phenol moiety exhibiting a pK_a value of 10.0 was selected as the precursor for the deprotonated anionic site that would be suitable for covalent-bond formation with the center carbon of the trityl unit. In addition, introduction of

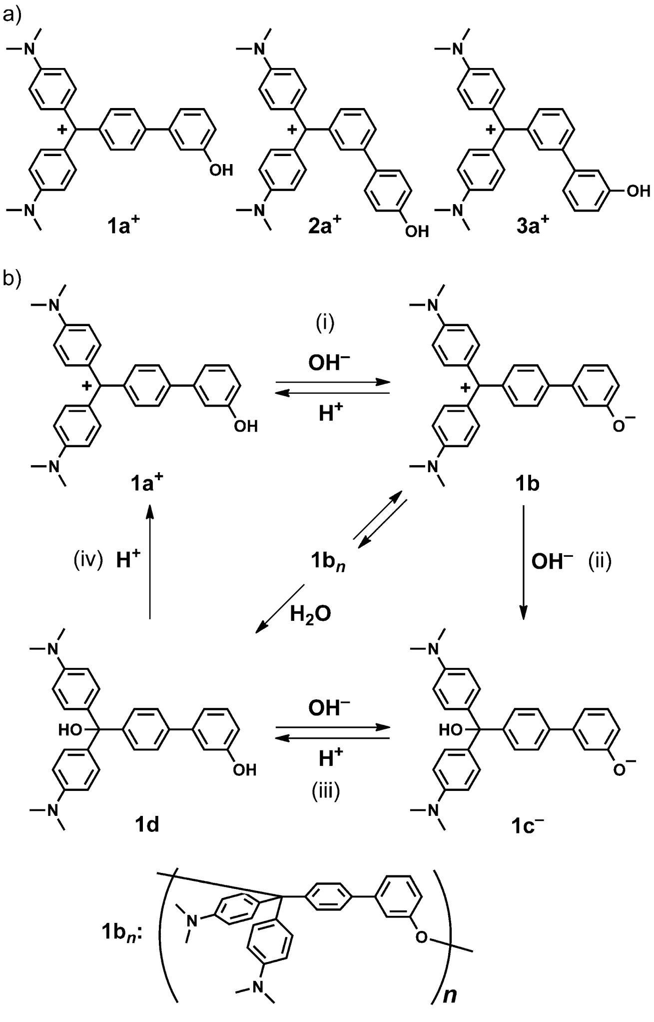

Figure 1. a) Trityl–phenol cationic species **1a**$^+$, **2a**$^+$, and **3a**$^+$ and b) representative example of the molecular structure changes of **1a**$^+$ as result of the addition of base (TPAOH) and acid (TFA).

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at least one *meta* linkage between the anionic and cationic sites was required to prevent the formation of less reactive quinoidal structures in derivatives with only *para* and *ortho* linkages.

Upon the addition of aqueous tetrapropylammonium hydroxide (TPAOH, up to 1 equiv) to a CH_3CN solution of $\mathbf{1a}^+\cdot BF_4^-$ (1.5 mM), the deep green color due to the trityl moiety of $\mathbf{1a}^+$ was gradually reduced to almost colorless, and turbidity was observed. This result initially suggested the formation of a covalent bond between the trityl carbon and the phenoxide (phenolate) oxygen as has been seen in oligomer and/or polymer states $\mathbf{1b}_n$ (*n* represents *n*mer(s), Figure 1 b, i). In this case, along with the solution containing oligomeric species, precipitates were formed due to the formation of polymers $\mathbf{1b}_{\mathbf{poly}}$. The pale green color in the precipitates can be explained by the trace amounts of terminal trityl units in the polymers. Further addition of TPAOH (1 equiv) resulted in a pale orange solution (Figure 1 b, ii). The UV/Vis absorption spectrum of $\mathbf{1a}^+$ in CH_3CN (1.5 mM) showed the disappearance of bands at $\lambda = 450$ and 622 nm and a concomitant increase in the band at 263 nm with the addition of one equivalent of TPAOH (Figure 2). These spectral changes were consistent with the quenching of the trityl-cation moiety by the base, resulting in the transformation of $\mathbf{1a}^+$ to $\mathbf{1c}^-$ through $\mathbf{1b}_n$ as oligomer and polymer structures, which seemed predominant in the equilibrium with zwitterion **1b**. Similar trends were observed in the UV/Vis absorption spectral changes ascribable to the formation of oligomers/polymers $\mathbf{2b}_n$ and $\mathbf{3b}_n$ from $\mathbf{2a}^+\cdot BF_4^-$ and $\mathbf{3a}^+\cdot BF_4^-$, respectively.

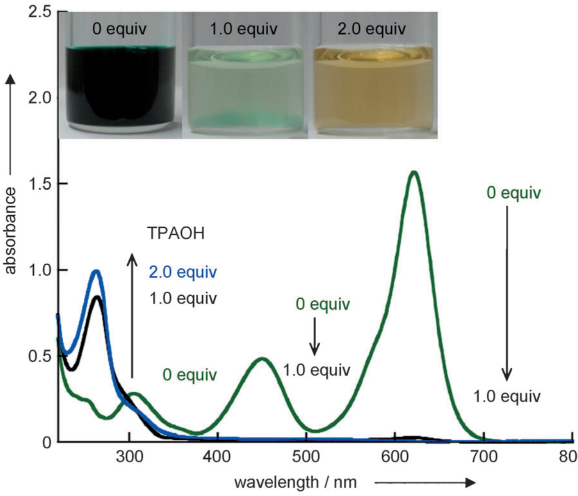

Figure 2. UV/Vis absorption spectral changes of $\mathbf{1a}^+\cdot BF_4^-$ in CH_3CN (1.5 mM) upon the addition of TPAOH and corresponding photographs of chromatic changes under visible light (inset). The precipitates were observed (as shown in the photograph of 1.0 equiv).

The oligomer soluble in CH_3CN as a main species was deduced to be a cyclic trimer $\mathbf{1b}_3$ by ESI-TOF-MS, exhibiting a distinct signal ascribable to the cationic complex with TPA^+ (Figure 3 a). Cyclic species derived from three zwitterionic monomers are of course electronically neutral and cannot be detected by ESI-MS. However, under the appropriate, but unusual conditions of significantly higher concentrations (>1 mM), the cyclic structures can interact with the TPA cation, which was added as the counterionic species of

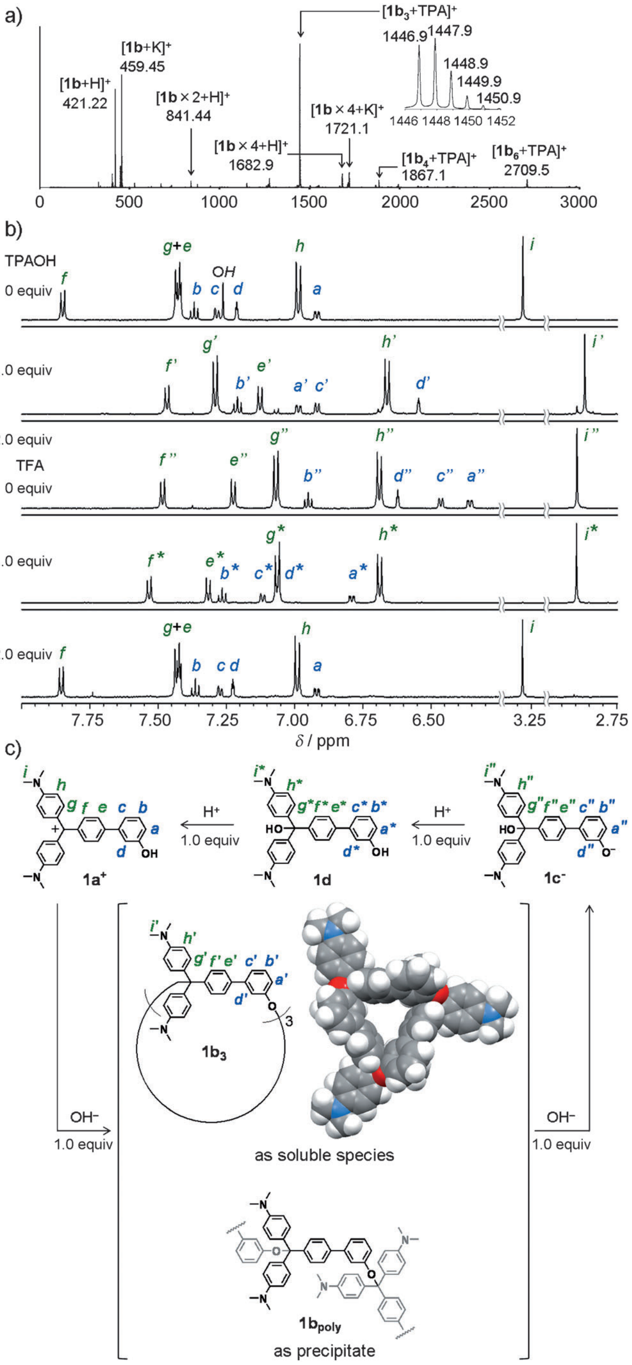

Figure 3. a) ESI-TOF-MS at a positive mode of soluble species $\mathbf{1b}_n$ as an CH_3CN solution (1.5 mM for the starting monomer) prepared from $\mathbf{1a}^+\cdot BF_4^-$ by the addition of 1.0 equiv of TPAOH, b) ^1H NMR spectral changes of $\mathbf{1a}^+\cdot BF_4^-$ in CD_3CN (1.5 mM) upon the addition of TPAOH and TFA, and c) corresponding states with proton labels in a Scheme along with the optimized structure of a cyclic trimer $\mathbf{1b}_3$ with a C_3 symmetry at B3LYP/6-31G(d,p).

the hydroxide, thus allowing the detection by ESI-MS. That is, the ionization was achieved by the complexation with tetraalkylammonium cations. On the other hand, the cyclic oligomers as cationic species by complexation with TPA were not detected from diluted solutions. In addition, dispersed polymers were also fabricated as precipitates along with cyclic oligomers that were soluble in CH_3CN, suggesting that the role of TPA as a template seems less effective.

Evidence for the formation of $\mathbf{1b_3}$ derived from the zwitterion **1b** was also provided by ^{1}H NMR spectral changes of $\mathbf{1a^+}$ upon the addition of TPAOH in CD_3CN (1.5 mM; Figure 3b and c). The species $\mathbf{1a^+}$, $\mathbf{1b_3}$, and $\mathbf{1c^-}$ were mainly observed in the presence of 0, 1.0, and 2.0 equivalents of TPAOH, respectively, whereas the zwitterion **1b** was not observed in the solution. For example, the proton H_f at $\delta = 7.85$ ppm, proximal to the cationic carbon, was shifted upfield to $\delta = 7.47$ and 7.48 ppm ($H_{f'}$ and $H_{f''}$) with 1.0 and 2.0 equivalents of TPAOH, respectively, suggesting that the cationic site disappeared upon the addition of OH^-. Furthermore, in contrast to the signal of phenol H_a of $\mathbf{1a^+}$ at $\delta = 6.92$ ppm, which was shifted downfield to $\delta = 6.99$ ppm ($H_{a'}$ of $\mathbf{1b_3}$) and upfield to $\delta = 6.36$ ppm ($H_{a''}$ of $\mathbf{1c^-}$) with 1.0 and 2.0 equivalents of TPAOH, respectively, the signal of phenol H_d of $\mathbf{1a^+}$ at $\delta = 7.21$ ppm was shifted upfield to $\delta = 6.55$ ppm ($H_{d'}$ of $\mathbf{1b_3}$) and downfield to $\delta = 6.63$ ppm ($H_{d''}$ of $\mathbf{1c^-}$) with 1.0 and 2.0 equivalents of TPAOH, respectively. These observations indicate that the phenol protons H_a and H_d of $\mathbf{1a^+}$ were deshielded and shielded, respectively, in $\mathbf{1b_3}$ (as $H_{a'}$ and $H_{d'}$) by aromatic rings made proximal through the formation of C–O covalent bonds, and that such effects were compensated in $\mathbf{1c^-}$ (as $H_{a''}$ and $H_{d''}$) by the removal of the proximal aromatic rings along with the emergence of an anionic phenoxide moiety. Addition of more than 1.0 equivalent of OH^- based on $\mathbf{1a^+}$ competed with the oligomerization and polymerization of the zwitterion **1b** by the nucleophilic attack of OH^- at the trityl cationic site. Interestingly, $\mathbf{1b}_n$, as the cyclic trimer and polymers, were gradually transformed to the monomeric diol **1d** by hydration in the solution state with water as the solvent for TPAOH. However, attempted dehydration of **1d** to form oligomer/polymers $\mathbf{1b}_n$ failed. This result suggests that the oligomer/polymers $\mathbf{1b}_n$ were kinetically produced as metastable states that could only be attained from a zwitterionic state. The diol **1d** was also obtained from $\mathbf{1c^-}$ by the addition of one equivalent of TFA (Figure 1b, iii), and addition of a second equivalent of TFA gave $\mathbf{1a^+}$ (Figure 1b, iv). In contrast to the behavior in CD_3CN, addition of TPAOH in protic CD_3OD solution provided the derivative substituted by a methoxy group at the trityl carbon without the formation of **1b** and $\mathbf{1b}_n$.

The formation of the cyclic trimer $\mathbf{1b_3}$ was also supported by diffusion-ordered spectroscopy (DOSY) in CD_3CN, exhibiting a diffusion constant of $7.99 \times 10^{-10}\,m^2s^{-1}$, which was slightly smaller than that of monomeric **1d** ($10.4 \times 10^{-10}\,m^2s^{-1}$). Furthermore, the deshielded and shielded signals of $H_{a'}$ and $H_{d'}$ by the formation of the covalent linkage in $\mathbf{1b_3}$ prepared from $\mathbf{1a^+}$ in the presence of one equivalent of TPAOH (Figure 2b) were correlated with the model structure of $\mathbf{1b_3}$ at the B3LYP/6-31G(d,p) level[8] (Figure 3c). In contrast, model structures of a cyclic dimer $\mathbf{1b_2}$ and a linear dimer as a polymer segment were not consistent with the observed symmetry features. By using ESI-TOF-MS, the soluble oligomers of $\mathbf{2b}_n$ and $\mathbf{3b}_n$ were also assigned as trimers $\mathbf{2b_3}$ and $\mathbf{3b_3}$, respectively, as main products soluble in CH_3CN solutions. Base- and acid-responsive ^{1}H NMR spectral changes similar to those of $\mathbf{1b}_n$ were observed in the formation and cleavage of $\mathbf{2b}_n$ and $\mathbf{3b}_n$. Furthermore, ^{1}H NMR integrals based on a TPA cation provided the precipitated polymer yields of 45%, 75%, and 19% for $\mathbf{1\,b_{poly}}$, $\mathbf{2\,b_{poly}}$, and $\mathbf{3\,b_{poly}}$, respectively, in CD_3CN (1.5 mM) as initial concentrations of cationic monomers. The yields depend on the polymerization conditions: a higher concentration at 6.0 mM for formation of $\mathbf{1\,b_{poly}}$ gave a value of 85%, suggesting that greater amount of polymer was formed in solutions with higher concentrations. Such concentration-dependent enhancement of the yields were also observed in $\mathbf{2\,b_{poly}}$ and $\mathbf{3\,b_{poly}}$.

Cyclic trimers were obtained preferentially over other cyclic oligomers, such as dimers and tetramers. As suggested by theoretical study,[8] cyclic trimers are more stable than the corresponding dimers and tetramers with strained conformations. Thus, the stabilities of cyclic trimers in solution were examined. Addition of one equivalent of TPAOH to the mixture of $\mathbf{1a^+}\cdot BF_4^-$ and $\mathbf{2a^+}\cdot BF_4^-$ (1:1, 1.5 mM in total) at room temperature in CD_3CN gave cyclic oligomers comprising two kinds of monomer units along with $\mathbf{1b_3}$ and $\mathbf{2b_3}$, according to their relative stabilities. Furthermore, the mixing of $\mathbf{1b_3}$ and $\mathbf{2b_3}$, which were prepared from $\mathbf{1a^+}\cdot BF_4^-$ and $\mathbf{2a^+}\cdot BF_4^-$ (1.5 mM in each), respectively, in CD_3CN resulted in similar results with the reaction starting from the mixture of $\mathbf{1a^+}$ and $\mathbf{2a^+}$; this indicates the exchange of constituent monomer units in these trimers. Although further examination was required for detailed information about the exchange mechanism, this observation suggested characteristic dynamic behaviors in these zwitterion-based covalent polymers.

Precipitates of $\mathbf{1\,b_{poly}}$, $\mathbf{2\,b_{poly}}$, and $\mathbf{3\,b_{poly}}$ were not soluble in various solvents due to their interpolymer interactions in the solid state, resulting in the difficulty in the studies on their structures in detail. Therefore, the precipitates prepared by casting the suspension in CH_3CN were examined by scanning electron microscopy (SEM) by using silicon substrates, and these results suggested the formation of organized structures (Figure 4). Compound $\mathbf{1\,b_{poly}}$ showed aggregates of flake-like structures with submicrometer-scale widths, whereas $\mathbf{2\,b_{poly}}$ and $\mathbf{3\,b_{poly}}$ formed partially linked spherical particles with approximately 100–200 nm diameters. The formation of the particles observed in $\mathbf{3\,b_{poly}}$ that are smaller than those observed in $\mathbf{2\,b_{poly}}$ correlated with the amounts of polymeric precipitates. The linkages between cationic and anionic sites were essential for determining the morphologies of polymeric structures. Furthermore, the precipitates of $\mathbf{1\,b_{poly}}$, $\mathbf{2\,b_{poly}}$, and $\mathbf{3\,b_{poly}}$ were hardly transformed to the cyclic oligomers in CD_3CN. The precipitates of $\mathbf{1\,b_{poly}}$,

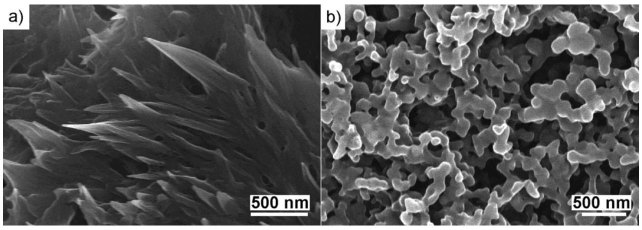

Figure 4. SEM images of a) **1 b**$_{poly}$ and b) **2 b**$_{poly}$ as precipitates prepared from CH_3CN (1.5 mm as initial concentrations of **1a**$^+$•BF_4^- and **2a**$^+$•BF_4^-, respectively) on silicon substrates.

2 b$_{poly}$, and **3 b**$_{poly}$ showed transitions by decomposition at 137, 170, and 180 °C, respectively, during heating. Synchrotron XRD analysis of **1 b**$_{poly}$, **2 b**$_{poly}$, and **3 b**$_{poly}$ as precipitates and after melting showed less and no ordered organized structures, respectively.[9]

The stimuli-responsive behavior of the zwitterion-based covalent polymers was examined. A characteristic property of the polymers was the fairly polarized C–O bond constructed by nucleophilic attack of the phenoxide oxygen as a strong base on the trityl carbon as a weak acid. Therefore, the C–O covalent bond had a relatively basic property, as was observed in salts consisting of weak acids and strong bases. In fact, even though **1 b**$_{poly}$ as a precipitate was stable in CD_3CN, treatment of **1 b**$_{poly}$ with CD_2Cl_2 as a solvent in the absence of water also gave cationic species, presumably due to degradation of CD_2Cl_2 by the basic polymers. In this case, the counteranionic species could not be identified precisely. On the other hand, the presence of water prevented such transformation in the polymers.[10] Therefore, appropriate molecules possessing polarized protic moieties could be associated with the polarized oxygen in the C–O linkage, resulting in bond cleavage. Such behavior is characteristic in macromolecules comprising ionic species due to their zwitterion-based covalent linkages.[11]

In summary, the first examples of zwitterion-based covalent oligomers and polymers exhibiting dynamic behaviors are reported, even though they did not always show the similar features as was observed in ordinary dynamic covalent polymers. Formation of the covalent polymers based on zwitterions does not follow ordinary polymerization mechanisms, such as anionic and/or cationic ones. Instead, the zwitterion-based polymers were formed through pre-polymerization, as was observed in supramolecular polymers,[12] because the monomer units have two reactive sites, cationic and anionic, in the initial state. Further modification of monomer units can control the stabilities of the oligomeric and polymeric structures and provide various functional materials, such as reversible photoresists, by mixing with photobase and photoacid generators. These detailed investigations are currently underway.

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[9] a) Various derivatives of zwitterion-based polymers can be fabricated. For example, cationic monomers **4a**$^+$, **5a**$^+$, and **6a**$^+$ as BF_4^- salts, which contain phenyl, biphenyl, and naphthyl moieties, respectively, in the spacer of **1a**$^+$ for constructing electronic materials, also gave **4b**$_{poly}$, **5b**$_{poly}$, and **6b**$_{poly}$ as precipitates in CH_3CN. The detailed-study manuscript is under preparation; b) dynamic behavior was also observed in the ^{1}H NMR spectra of the mixture of **1b**$_3$ and **4b**$_3$, prepared from **1a**$^+$·BF_4^- and **4a**$^+$·BF_4^- (1.5 mM in each), respectively, in CD_3CN, along with ESI-TOF-MS.

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