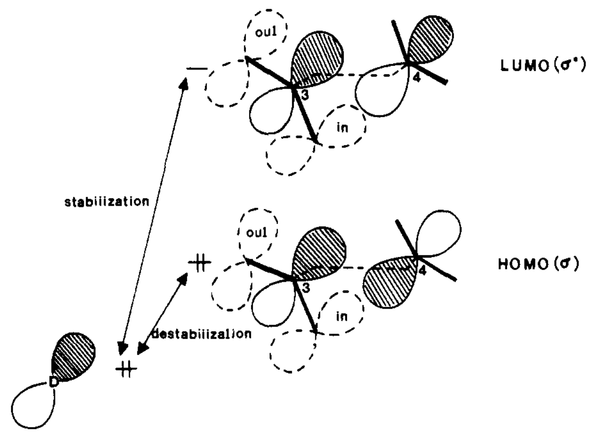

Figure 2. HOMO and LUMO of the cyclobutene transition structure and the occupied p orbital of a donor orbital. The positions that a donor substituent orbital assumes upon inward or outward rotation are shown by the dashed lines.

structures, and products were fully optimized at the RHF level using the 3-21G basis set[10] and analytical energy gradients.[11] The transition structures and calculated activation energies are shown in Figure 1.[12] The transition structure for the cyclobutene–butadiene interconversion agrees closely to that obtained by Breulet and Schaefer at a higher level.[13] The activation energy at the 3-21G level is 9 kcal/mol too high (7.6 kcal/mol with zero-point energy corrections) but becomes only 0.3 kcal/mol too high when MP2 correlation energy corrections are made. The 3-21G activation energies for the other reactions in Figure 1 are all about 10 kcal/mol too high as compared to experimental data or to estimates based upon the substituent additivities given in Table II (with hydroxy used as a model for alkoxy). This error is due to the neglect of correlation energy, which stabilizes the transition structures more than the reactants and is similar to that found in 3-21G calculations on sigmatropic shifts.[14]

The large difference between the activation energies for the outward and inward rotations of hydroxy groups in *trans*-3,4-dihydroxycyclobutene is not a result of steric repulsion upon inward rotation but can be understood by examining the interactions between the frontier molecular orbitals of the cyclobutene transition structure and the occupied p orbital of a donor substitutent. In the transition structure for a conrotatory electrocyclization, the HOMO of cyclobutene is essentially a distorted σ orbital, while the LUMO is a σ^* orbital.[15] These are sketched in Figure 2. Upon outward rotation of a donor substituent, the donor orbital can mix with the LUMO, resulting in stabilization and lowering of the activation energy. This is only partially counteracted by the destabilizing four-electron interaction of the donor orbital with the distorted cyclobutene HOMO. Because of the location of the donor orbital upon outward rotation (shown by the dashed lines labeled "out"), the donor orbital overlaps primarily with the atomic orbital at C_3.

Upon inward rotation, the donor orbital will move into the location marked by the dashed orbital labeled "in". In this location the donor orbital overlaps with the atomic orbitals at both C_3 and C_4. The interaction of an inwardly rotating donor orbital with the distorted cyclobutene LUMO is less than that of an outwardly rotating donor orbital, because the signs of the neighboring lobes of the atomic orbitals at C_3 and C_4 are opposite. Consequently, stabilization upon inward rotation of the donor is less than upon outward rotation. At the same time, the donor orbital overlaps more with the distorted cyclobutene HOMO upon inward rotation than upon outward rotation, due to overlap at both C_3 and C_4. This destabilizing interaction is larger for inward rotation than outward rotation. Thus, both interactions favor outward rotation, and the extent of this preference depends upon the donor ability of the substituent. With π-acceptor substituents, orbital interactions also occur between the HOMO of cyclobutene and the empty orbital of the acceptor. This two-electron stabilizing interaction is maximized when the acceptor rotates inward and may cause acceptors to preferentially rotate inward. Experimentally, acceptors show little preference for inward and outward rotation.[2]

Substituent effects of this type should influence other pericyclic reactions, such as disrotatory 6π-electron electrocyclizations, and may influence the overall stereochemistry of isomerizations of cyclopropanes[16] and related molecules.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research, to the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award to K.N.H., which made this collaboration possible, and to Professor William R. Dolbier for enlightening discussions.

Registry No. Cyclobutene, 822-35-5; 3-methylcyclobutene, 1120-55-4; *cis*-3,4-dimethylcyclobutene, 1517-14-2; *trans*-3,4-dimethylcyclobutene, 1517-13-1; 3-chlorocyclobutene, 93280-82-1; *cis*-3,4-dichlorocyclobutene, 2957-95-1; *trans*-3,4-dichlorocyclobutene, 1192-02-5; *cis*-3-chloro-4-methylcyclobutene, 93280-83-2; 3-acetoxycyclobutene, 27238-02-4; 3-ethoxycyclobutene, 93280-84-3; *cis*-3,4-diethoxycyclobutene, 93280-85-4; *cis*-3,4-dimethoxycyclobutene, 67520-63-2; *cis*-3-chloro-4-methoxycyclobutene, 67520-62-1; *cis*-3-methoxy-4-methylcyclobutene, 93280-86-5; methyllithium, 917-54-4; 1-chloro-3-ethoxycyclobutane, 93280-87-6.

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Novel Polyelectrolyte Composites That Yield Polycationic Electrode Coatings with Large Ion Exchange Capacities and Exceptionally High Effective Diffusion Coefficients for Incorporated Counterions

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The use of adherent polyelectrolytes to bind counterionic reactants to electrode surfaces has grown in popularity since this tactic was first demonstrated with poly(4-vinylpyridine).[1] Despite the variety of reports in which polyelectrolyte-coated electrodes have been exploited,[2-4] the number of polyelectrolytes suitable for preparing stable electrode coatings remains relatively small. Most commonly available ionic polymers are either too soluble or undergo facile counterion exchange so that incorporated ionic reactants are rapidly lost from electrode coatings.

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[⊥] Contribution No. 7089.

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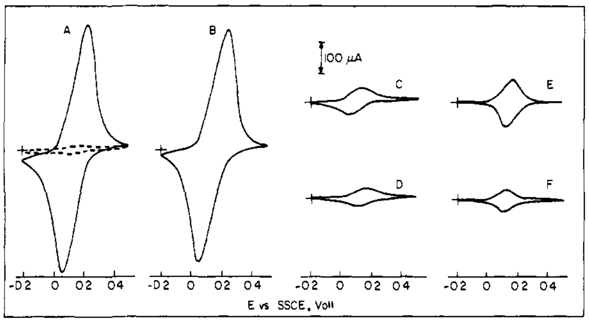
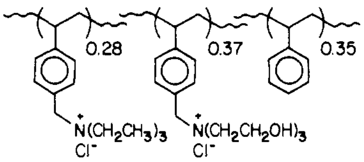


Figure 1. Steady-state cyclic voltammograms for $Fe(CN)_6^{4-}$ incorporated in simple and composite polyelectrolyte coatings on a glassy carbon electrode (0.34 cm^2). Each coating was equilibrated with 10^{-4} M $Fe(CN)_6^{4-}$ in 0.1 M acetate buffer (pH 4.5) until there were no further changes in the cyclic voltammetric response (5–10 min). Coating compositions, as specified in Table I: (A) PVI + I, (B) 45 min after transfer to pure supporting electrolyte, (C) I alone, (D) as in (B), (E) PVI alone, (F) as in (B). The dashed curve in (A) is the response for 10^{-4} M ($Fe(CN)_6^{4-}$ at the uncoated electrode. Scan rate: 100 mV s^{-1}.

We have observed that a new composite coating material, consisting of a mixture of a random ternary copolymer containing positively charged sites, with any one of a series of cationic homopolymers produces stable electrode coatings with properties that are superior to those of any previously described material: (i) Large quantities of counterionic reactants are incorporated by the composite coatings and are retained for extended periods. (ii) The incorporated reactants are able to diffuse rapidly within the coatings so that unusually high current densities for their oxidation and reduction can be realized. This combination of properties has been difficult to achieve with previously described coating materials, but they are essential in applications where the incorporated reactants are to serve as electrocatalysts or redox mediators. For this reason, among others, the composite coating approach appears to offer particular promise.

The key ingredient in the preparation of the composite polyelectrolyte mixtures was the random ternary copolymer I. The



I

composition of the material employed, shown in the formula, was selected to provide a combination of hydrophilic and hydrophobic groups with the aim of achieving extensive swelling of the coatings while maintaining good adherence to the electrode surface.[5] Electrode coatings were cast by mixing 1 µL of I (0.5 wt % in aqueous THF) with 1 µL of the cationic homopolymer (0.5 wt % in methanol) and depositing the mixture on the surface of a glassy carbon electrode (0.34 cm^2). After the solvents had evaporated (ca. 30 min at 22 °C) the coated electrode was transferred to aqueous acetate buffer solutions (pH 4.5) to carry out various electrochemical measurements as described previously.[6]

The ability of a typical composite coating to incorporate and retain large quantities of $Fe(CN)_6^{4-}$ anions is demonstrated with cyclic voltammograms A and B in Figure 1. Over 90% of the $Fe(CN)_6^{4-}$ initially incorporated by the hybrid coating is retained after 45 min of soaking in pure supporting electrolyte. (The 45-min period was chosen only for experimental convenience. The $Fe(CN)_6^{4-}$ leaves the coating very slowly at longer times, e.g., 71% was retained after 36 h.) This behavior contrasts sharply with that of coatings prepared from either one of the two components of the composite coating. Thus, the smaller peak currents of curves C and E in Figure 1 reflect the much smaller quantities of $Fe(CN)_6^{4-}$ that are incorporated by coatings prepared from either one of the polyelectrolytes present in the composite coating used to record curves A and B. Voltammograms D and F show that transfer of these loaded coatings to pure supporting electrolyte leads to substantial loss of $Fe(CN)_6^{4-}$ within 45 min (Table I).

Table I. Diffusion Coefficients and Retention Ratios for $Fe(CN)_6^{4-}$ Incorporated in Electrode Coatings Prepared from Simple and Composite Polyelectrolytes

coating material[a]	$10^7\Gamma_p$,[b] mol cm^{-2}	$10^8\Gamma_0$,[c] mol cm^{-2}	Γ_{45}/Γ_0[d]	10^6D_E,[e] $cm^2\ s^{-1}$
PVI[f]	1.55	0.39	0.54	[g]
PVP[h]	5.37	10.3		0.0038[i]
I	0.45	0.37	0.73	[g]
PVI[f] + I	1.99	2.40	0.93	1.6
PVP[h] + I	1.85	2.27	0.84	1.4
PVP[f] + I	1.85	2.32	0.82	1.2
ND + 1	1.39	2.18	0.88	1.5

[a] Abbreviations: PVI = poly(*N*-vinylmethylimidizole); PVP = poly(4-vinylpyridine); ND = nylon derivative, $-(NHC(=O)-)(CH_2)_4CH(N(CH_3)_2)-_n$. [b] Total quantity of cationic sites in the polyelectrolyte coating. [c] Quantity of $Fe(CN)_6^{4-}$ incorporated by the coating upon equilibration with a 10^{-4} M solution of $Fe(CN)_6^{4-}$ in 0.1 M acetate buffer at pH 4.5 as measured coulometrically immediately after transfer to pure supporting electrolyte solution. [d] Retention ratio: fraction of the initially incorporated $Fe(CN)_6^{4-}$ that was retained 45 min after the coated electrode was transferred to 0.1 M acetate buffer (pH 4.5). [e] Effective diffusion coefficient of $Fe(CN)_6^{4-}$ in the coating as measured chronocoulometrically.[6] [f] Molecular weight, 70 000. [g] D_E not evaluated because of uncertainty in coating thickness. [h] Molecular weight, 750 000. [i] D_E evaluated in 0.1 M CF_3COONa at pH 1.8.[10]

The voltammograms in Figure 1 reveal the synergistic effect on the incorporation capacity and retention ability that results when the two polyelectrolytes are mixed to produce a composite coating. The magnitude of the effect is demonstrated by comparing the entries in column 3 of Table I for mixtures of I with several auxillary polyelectrolytes with those for the two common homopolyelectrolytes. The fractions of the initially incorporated $Fe(CN)_6^{4-}$ that are retained after 45 min of soaking in pure supporting electrolyte are also given. In every case, the composite coating incorporates and retains substantially more $Fe(CN)_6^{4-}$ than would be anticipated from the behavior of either component alone. It is also noteworthy that, of the homopolyelectrolytes used to form the composite coatings listed in Table I, only PVI forms coatings with sufficient stability under our experimental conditions to permit reliable measurements of electrochemical responses.

The composite coatings exhibit still another desirable property: unusually large effective diffusion coefficients, D_E,[7] for the incorporated, multiply charged anions. Some values of D_E, measured by standard electrochemical techniques,[6,8] are listed in Table I. Micrometer measurements of coatings prepared from 10 times more material than actually used experimentally were divided by 10 to give the coating thickness required for evaluation of D_E; for composite coatings in Table I the values of D_E range from 1.2×10^{-6} to 1.6×10^{-6} $cm^2\ s^{-1}$. These are the largest values of D_E ever reported for multiply charged counterions bound electrostatically within polyelectrolyte coatings. That they are observed for the same coatings that exhibit the retention ratios listed in Table I is surprising. It implies that the $Fe(CN)_6^{4-}$ counterions move much more rapidly within the electrostatic Donnan domains[9] than into and out of them.

We believe the remarkable properties of the composite coatings result from the ability of polyelectrolyte I to serve as a template that determines the morphology of all of the composite coatings

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(5) I was prepared by conventional free-radical copolymerization of styrene and chloromethylstyrene followed by functionalization with the appropriate amines by means of the Menschutkin reaction. Its composition was determined by elemental analysis and IR spectroscopy.

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in Table I despite the differences in the second polyelectrolyte present. Since the properties exhibited in isolation by coatings of I or of the auxillary homopolyelectrolytes are distinctly different and less attractive than those of the composite coatings the morphology of the coatings appears to be the dominant factor controlling their behavior. Transmision electron microscopic evidence supporting this proposal along with considerable additional experimental details are described in the full paper.

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Registry No. $(\text{-NH(CH}_2)_4\text{CH(N(CH}_3)_2)\text{CO-})_n$ (SRU), 75855-87-7; PVI (homopolymer), 26983-77-7; PVP (homopolymer), 25232-41-1.

Distinction between Aminium Cation Radical and Protic Acid Catalyzed "Diels-Alder" Reactions

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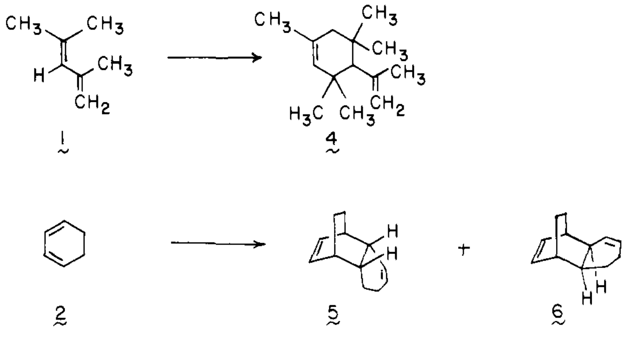
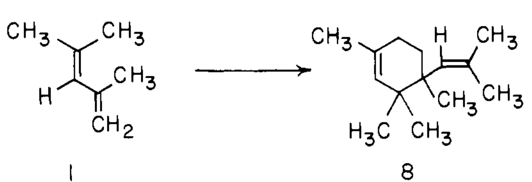
Recently, we reported[2] that certain intramolecular "Diels-Alder" reactions could be catalyzed by both aminium cation radicals[3,4] and protic acids.[5] In that report[2] we stressed the striking similarity of the cation radical and protic acid promoted processes and questioned whether the addition of an aminium cation radical to the reaction mixture was merely leading to the generation of a protic acid, which was the true catalytic species. In order to test this concept and to extend our earlier work from intramolecular to intermolecular 2 + 4 cycloadditions, we have examined, in detail, the dimerization of 2,4-dimethyl-1,3-pentadiene (**1**) and 1,3-cyclohexadiene (**2**) as catalyzed by tris(*p*-bromophenyl)aminium hexachloroantimonate (**3**).[3,4] We now wish to report that certain cation radical promoted Diels-Alder reactions can be readily distinguished from the corresponding protic acid catalyzed processes and that the previously reported[3b] dimerization of **1** is a protic acid catalyzed reaction and not a cation radical induced process as previously claimed.[3b] Lastly, we have found that the true cation radical dimerization of **1** is a relatively slow process, which leads to an entirely different dimer from that formed in the protic acid catalyzed process. These findings, when applied to other examples, will constitute a test for distinguishing between single-electron-transfer (cation radical) and protonation (protic acid induced) mechanisms for certain reactions.

Treatment of either **1** or **2** with 5 mol % of the cation radical **3** in methylene chloride produced the Diels-Alder dimers 1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexene (**4**) and a mixture of **5** and **6**, respectively, in high yield as previously reported.[3a,b] However, the similarity of these reactions stops at this point. The dimerization of **1** to give **4** could be accomplished in 95% yield using either **3**[3b] or hydrogen bromide[5] as the catalyst. In matched reactions using **3** and hexachloroantimonic acid ($HSbCl_6$),[6] we obtained an 88% yield of **4**. In contrast, attempts to catalyze the conversion of **2** into **5** and **6** with protic acid gave large amounts of intractable material and only trace amounts of **5** and **6** after prolonged periods.


1 **4** **2** **5** **6**

With 5 mol % of **3** as catalyst, the dimerization of **1** showed an induction period at -42 °C. This induction period was significantly increased in base-washed glassware or in the presence of 1 mol % of 2,6-di-*tert*-butylpyridine (**7**).[7] When 2,6-di-*tert*-butylpyridine was added in amounts greater than **3**, the formation of **4** from **1** was completely inhibited even though the aminium cation radical **3** was present in the reaction mixture. For example, when 20 mol % of 2,6-di-*tert*-butylpyridine was present in a reaction mixture containing **1** and 5 mol % of **3** at -23 °C, no trace of **4** could be detected even though the blue color of the aminium cation radical persisted for 20 min. In the absence of the base, **1** was completely converted into **4** in 2 min under these conditions. In contrast to the findings with **1**, the dimerization of **2** proceeded to 27% yield with 62% of the starting material being unreacted in the presence of 20 mol % of 2,6-di-*tert*-butylpyridine at 0 °C in 90 s, at which time the blue color of **3** disappeared and the reaction stopped.[7] Thus, the observed reaction of **1** was inhibited by base, while that of **2** was not.

Our observations on the dimerization of 1,3-cyclohexadiene were consistent with the cation radical chain mechanism proposed in the literature.[3a] In contrast, the results observed for the reactions of **1** were consistent with a protic acid catalyzed process but not with a cation radical chain process.[8] This suggested to us that we should determine if **1** could be dimerized in a cation radical chain process and if the product would be **4** or some other product resulting from a cation radical induced transformation. When **1** was treated with 50 mol % of **3** and 55 mol % of 2,6-di-*tert*-butylpyridine at 25 °C, a new dimer, **8**, was obtained in 27% yield.[11] Similarly, irradiation of a 0.5 M solution of **1** in ace-


1 **8**

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[7] 2,6-Di-*tert*-butylpyridine does not react at a significant rate with **3** by itself, as analyzed by visible absorption spectroscopy. However, it does accelerate the rate of decomposition of **3** in the presence of **1** or **2**, presumably by removing protons from cation radicals generated in the reaction of **1** or **2** with **3**.

[8] We wish to stress that the protic acid could originate from loss of protons from initially generated cation radicals[9] or from dimerization of cation radical intermediates followed by proton loss.[10]

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