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Intramolecular Compartmentalization of Photoredox Centers in Functionalized Amphiphilic Polyelectrolytes: A Model for Collisionless Electron Transfer Systems

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ABSTRACT: Photoactive centers (phenanthryl groups) covalently linked to a polyanion were "compartmentalized" in the hydrophobic aggregates of pendant phenyl groups covalently incorporated in the polyanion. In this amphiphilic polyanion, a collisionless long-range electron transfer occurs from photoexcited phenanthrene (Phen) moieties to methylviologen (MV^{2+}) bound electrostatically as well as hydrophobically to the peripheral area of the hydrophobic aggregates. Backreaction also takes place in a collisionless process. Without pendant phenyl groups, the Phen residues tend to form ground-state charge-transfer (CT) complexes with MV^{2+}, which highly disfavor the photochemical production of $MV^{\bullet +}$. As a result of the compartmentalization, the CT complexation with MV^{2+} was suppressed while the Phen fluorescence quenching was enhanced, leading to a considerable increase in the photochemical yield of $MV^{\bullet +}$. An important observation was that the back electron transfer was slower than the forward reaction by a factor of at least 10^3, which may be explicable in terms of the "inverted region" of electron transfer theory proposed by Marcus and others. Pendant lauryl chains in place of phenyl groups were found to be ineffective in compartmentalizing the Phen moieties presumably because the aggregates of long alkyl chains are loose as compared to those of aromatic rings that tend to stack tightly in the aggregates.

Introduction

For an understanding of the fundamental aspect of collisionless electron-transfer reactions that are known to be operating in biological photosynthetic systems,[1] considerable interest has been directed toward simple model systems in which electron donors and acceptors are tightly held in fixed distances so that no diffusional encounter of the reactants is allowed. These model systems include rigid matrix systems, wherein the reactant molecules are buried in separation,[2] and linked donor–acceptor molecules with a rigid spacer.[3] A large number of studies have also focused on electron-transfer processes across the interfaces of some organized assemblies such as surfactant micelles and vesicles, where some particular donors and acceptors are expected to reside separately with respect to a phase boundary. However, in these interfacial systems, it is difficult to fix the reactants in a specific location because of the dynamic nature of the systems.

Amphiphilic polyelectrolytes have been demonstrated to form organized structures as a result of intramolecular microscopic phase separations in aqueous media consisting of aggregates of the hydrophobic residues and of charged interfaces.[4-6] Previous papers have shown that an amphiphilic copolymer of 9-vinylphenanthrene (9VPh) and 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) behaves as an unimolecularly organized assembly with photochemical functionality.[7-11] Phenanthrene (Phen) residues covalently linked to the amphiphilic copolymer form a tight ground-state complex with methylviologen (MV^{2+}) as a consequence of electrostatic, hydrophobic, and

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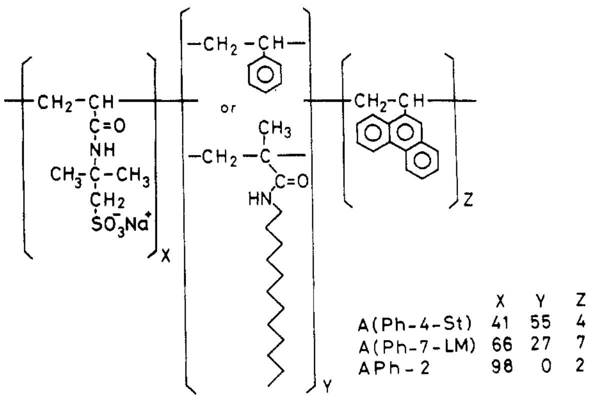
Scheme I



	X	Y	Z
A(Ph-4-St)	41	55	4
A(Ph-7-LM)	66	27	7
APh-2	98	0	2

ground-state charge-transfer (CT) interactions exerting together in a cooperative manner.[8,10] Importantly, however, the CT complex is photochemically inactive in reduction of MV^{2+}, because efficient electron transfer occurs in the complex, but extremely rapid back reaction prevents the production of reduced viologen ($MV^{\bullet +}$).[10] These findings have prompted us to modify the amphiphilic polyelectrolytes in such a way that the Phen residues are "compartmentalized" in a macromolecular microenvironment so that the CT interaction of the Phen residues with MV^{2+} is hindered but a collisionless long-range electron transfer from the excited Phen to MV^{2+} remains possible.

In the present study we synthesized amphiphilic polyanions consisting of a relatively small amount of the Phen groups as a photoredox center and phenyl rings or lauryl chains as additional hydrophobic pendant groups to form hydrophobic aggregates (Scheme I). We expected that the hydrophobic microdomains would hydrophobically incorporate the Phen groups, thereby the photoredox centers being compartmentalized. In the CT complex between Phen and MV^{2+}, the pyridinium rings of MV^{2+} are considered to retain a face-to-face orientation against the phenanthrene ring in contact with each other.[10] Therefore, it is conceivable that the surrounding hydrophobic pendant groups can prevent a close approach of MV^{2+} to the Phen sites, and hence the rigorous orientation for the CT complexation would be hindered. Since the requirements for the distance and orientation for electron transfer may not be so rigorous as those for the CT complexation,[2,3] efficient photoredox reactions may still occur between the photoexcited Phen and MV^{2+} in such a situation. This type of amphiphilic polyelectrolytes may provide a useful, simple model system where a collisionless electron transfer can occur with acceptors bound in the peripheral areas of the hydrophobic aggregates.

Experimental Section

Materials. 9-Vinylphenanthrene (9VPh) was synthesized as reported previously.[7] Laurylmethacrylamide (LMA) was synthesized from acryloyl chloride and dodecylamine. The details of the synthesis will be reported elsewhere.[13] 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) was a gift from Nitto Chemical Industry Co. and used without further purification.

Methylviologen (Tokyo Kasei Co.) was purified by recrystallization from an aqueous solution containing a small amount of acetone. Water was doubly distilled and deionized by passing through an ion-exchange resin column.

Polymerizations. The terpolymer of AMPS, styrene, and 9VPh [A(Ph-4-St)] was synthesized as follows: An ampule containing 5.4 g (26.4 mmol) of AMPS, 0.3 g (1.46 mmol) of 9VPh, 1.8 g (17.6 mmol) of styrene, 2.9 mg (0.18 mmol; 0.4 mol % on the basis of the total monomers) of 2,2′-azobis(2-methylpropionitrile) (AIBN), and 50 mL of *N*,*N*-dimethylformamide (DMF) was outgassed on a vacuum line by five freeze–pump–thaw cycles and then sealed under vacuum. Polymerization was carried out at 60 °C for 20 h. The mixture was poured into a large excess of ether to precipitate the resulting polymers. The polymers were then dissolved in dilute aqueous sodium hydroxide and the solution was dialyzed against pure water for 5 days and lyophilized: yield 1.15 g (15.3% conversion). The composition of the terpolymer was calculated by the combined use of the IR spectra and the C/N ratio: The mole ratio of AMPS and styrene was determined by the IR spectra using the 700-cm^{-1} and 1200-cm^{-1} bands associated with the benzene ring and the sulfonate group, respectively, as the key bands. The calibration curve for the IR analysis was obtained by using the copolymers of AMPS and styrene with various compositions prepared in the previous study.[4]

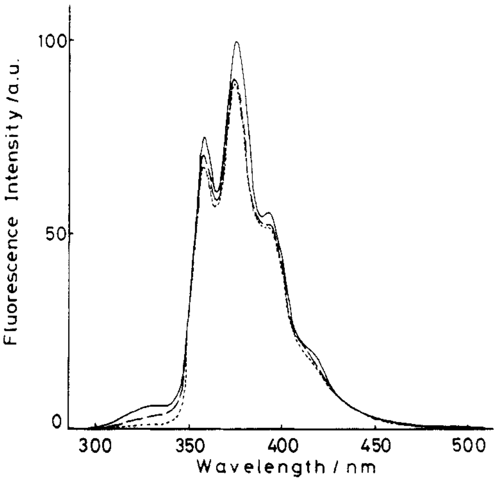


Figure 1. Fluorescence spectra measured in aqueous solutions at room temperature: (—) A(Ph-4-St); (- - -) A(Ph-7-LM); (— — —) APh-2; [Phen](residue) = 0.33 mM; excitation wavelength, 297 nm.

The terpolymer of AMPS, LMA, and 9VPh [A(Ph-7-LM)] was prepared analogously from a mixture of 3.1 g (14.8 mmol) of AMPS, 0.1 g (0.49 mmol) of 9VPh, 1.75 g (6.9 mmol) of LMA, 0.05 g (0.5 mmol) of triethylamine (TEA), 18.2 mg (0.11 mmol; 0.5 mol % on the basis of the total monomers) of AIBN, and 30 mL of THF. The polymers precipitated in an excess of ether were dissolved in dilute sodium hydroxide, and liberated TEA was removed by shaking with *n*-hexane 3 times. The aqueous solution was dilayzed against pure water for 10 days and then lyophilized: yield 0.21 g (4.2% conversion). The composition of the terpolymer was determined by the C/N and C/S ratios of microanalysis.

The copolymer of AMPS and 9VPh (APh-2) was prepared as reported previously.[11]

Measurements. Fluorescence spectra were recorded on a Shimazu RF-02A spectrofluorimeter.

Fluorescence decay data were obtained by using a correlated single-photon counting system at the University of Texas at Austin. A mode-locked, frequency-tripled (355 nm) Nd:YAG laser was used as the excitation source. Fluorescence decay function was deconvoluted with the system response function, and the parameters of the multiexponential decay function were varied until the best least-squares agreement with the data was obtained.

Laser photolysis was carried out by using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at the third harmonic (150 mJ per flash at 355 nm with a 6-ns fwhm). An analyzing beam from a 150-W xenon arc lamp was set perpendicular to the laser beam, and a Hamamatsu R928 photomultiplier tube was used as a detector combined with an Iwatsu D901 transient memory (sample rate, 10 ns) and an NEC PC9801F microcomputer for data acquisition. For faster events, the output from the photomultiplier tube was directly recorded on a Textronix 485 type oscilloscope for a photographical analysis. In some cases, fluorescence decay traces were recorded on the same system. Sample solutions were deaerated by bubbling with nitrogen for 30 min immediately before use.

Results and Discussion

The amphiphilic polyanions employed in the present study were illustrated in Scheme I. The fluorescence

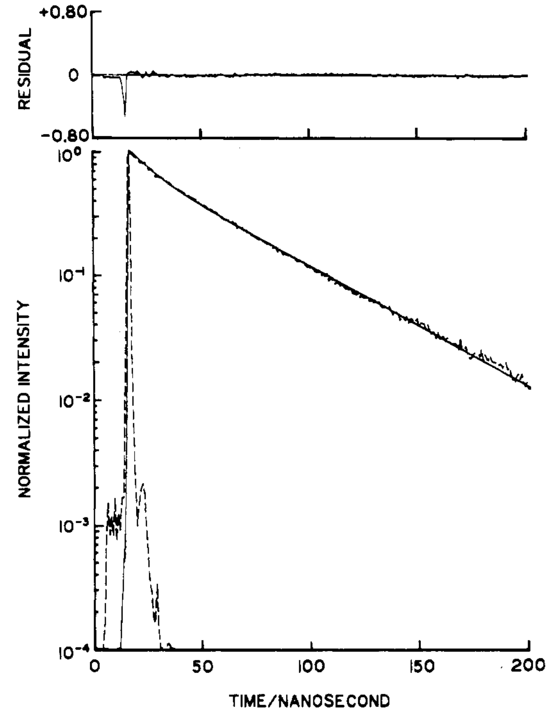


Figure 2. Fluorescence decay trace for A(Ph-4-St) in an aqueous solution. The decay curve was best fitted to double-exponential function $I(t) = 0.304 \exp(-t/10.1\ (\mathrm{ns})) + 0.696 \exp(-t/44.7\ (\mathrm{ns}))$. Average lifetime (defined as $\langle \tau \rangle = \sum a_i\tau_i^2/\sum a_i\tau_i$) is 42 ns.

Table I
Photochemical Data for the Amphiphilic Polyanions

polymers	$\langle \tau \rangle$,[a] ns	K_{CT},[b] 10^2 M^{-1}	K_{SV},[c] 10^3 M^{-1}	k_q,[d] 10^{10} M^{-1} s^{-1}	k_b[e]
A(Ph-4-St)	42	2.1	16	38	4.4×10^4 s^{-1}
A(Ph-6-LM)	39	11	26	67	3.2×10^4 s^{-1}
APh-2	35	5.1	3.1	8.9	3×10^{10} M^{-1} s^{-1}

[a] Average lifetime of fluorescence. [b] Apparent CT formation constants estimated from the Scott plots (see inserts in Figure 4). [c] Apparent Stern–Volmer constants estimated from the initial slopes of the quenching curves (Figure 2). [d] Second-order equivalent quenching rate constants calculated from the K_{SV} values and average lifetimes of fluorescence. [e] Back electron transfer rate constants estimated from the linear portions of the kinetic plots on the microsecond time scale (see text).

spectra of the aqueous solutions of A(Ph-4-St), A(Ph-7-LM), and APh-2 are compared in Figure 1. The Phen groups in A(Ph-4-St) and A(Ph-7-LM) are expected to exist in the hydrophobic microenvironments of the polymers, while those in APh-2 are known to be exposed to an aqueous phase.[11] However, the differences among the fluorescence spectra for these polymers are small. This is due in part to the fact that, unlike the pyrene case,[14] the phenanthrene fluorescence per se is not sensitive to the polarity of media and in part to the absence of singlet-state–ground-state interactions that often occur in the case of polymers with high loadings of the Phen groups.[7,11] The steady-state fluorescence intensity of A(Ph-4-St) was slightly higher than those of APh-2 and A(Ph-7-LM). Figure 2 shows a fluorescence decay profile of A(Ph-4-St) in an aqueous solution. The decay curve was not single exponential but was best fitted to a double-exponential function. The same was true for the APh-2 and A(Ph-7-LM) systems. The decay profiles for these three polymers were similar except the average lifetime for A(Ph-4-St) was a little longer than those of APh-2 and A(Ph-7-LM) (Table I). These observations suggest that the Phen moieties in A(Ph-4-St) are more isolated from one another in macromolecular environments than are the cases for APh-2 and A(Ph-7-LM) as will be discussed later.

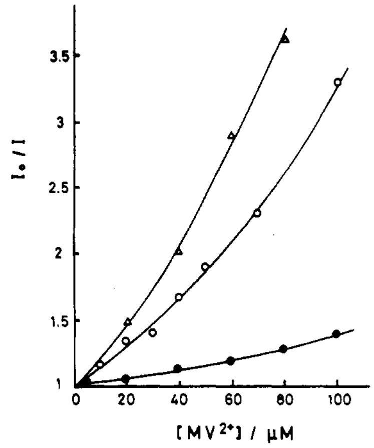


Figure 3. Stern–Volmer-type plots for the Phen fluorescence quenching by MV^{2+} in aqueous solution: (○) A(Ph-4-St); (△) A(Ph-7-LM); (●) APh-2; [Phen](residue) = 0.26 mM; excitation wavelength, 297 nm.

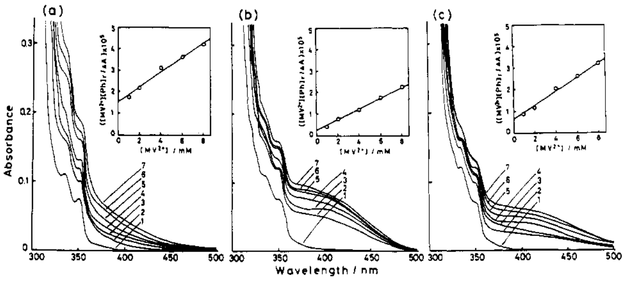


Figure 4. Absorption spectral changes of aqueous solution of (a) A(Ph-4-St), (b) A(Ph-7-LM), and (c) APh-2 upon addition of various amounts of MV^{2+}: [Phen](residue) = 0.245 mM; [MV^{2+}], (1) 0, (2) 0.5, (3) 1.0, (4) 2.0, (5) 4.0, (6) 6.0, and (7) 8.0 mM. Inserts: Scott plots for the data.

Upon addition of methylviologen, the fluorescence was quenched quite effectively as a result of electron transfer from the singlet excited state of the Phen residues to MV^{2+}. The relationships between the relative fluorescence intensities (I_0/I) and the quencher concentrations were plotted in Figure 3, where I_0 and I are the Phen fluorescence intensities in the absence and presence of the quencher. Being a cationic species, MV^{2+} would be bound to the negatively charged macromolecular environment, leading to a close proximity of the quencher and the Phen moieties.[8] Hence, the steady-state quenching data do not fit simple Stern–Volmer kinetics, giving rise to a static nature in the quenching. It is noteworthy that the quenching for the A(Ph-7-LM) and A(Ph-4-St) systems exhibited a very high efficiency and a marked curve upward with an increase in the MV^{2+} concentration as compared with that for the APh-2 system. The apparent Stern–Volmer constants (K_{sv}) estimated from the initial slopes of the plots in Figure 2 and the apparent second-order equivalent rate constants are listed in Table I. These results suggest that both the lauryl chains in A(Ph-7-LM) and the phenyl rings in A(Ph-4-St) exist in aggregation in aqueous solutions and that a number of the MV^{2+} dications are associated with the aggregates through electrostatic as well as hydrophobic interactions.[8] It should be noted here that, by contrast, APh-2 exists in an extended chain conformation in aqueous solution as reported previously.[11]

As mentioned earlier, Phen residues covalently linked to polyanions easily form CT complexes with MV^{2+} in aqueous solutions.[8] Figure 4 shows the changes in the absorption band tails of the Phen chromophores in aqueous solutions upon addition of MV^{2+}. If the MV^{2+}

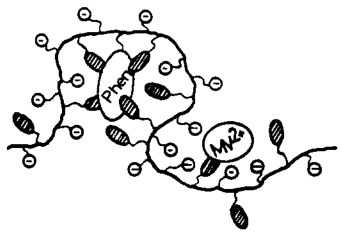


Figure 5. Conceptual illustration of "compartmentalization" of Phen chromophores by aggregates of pendant phenyl groups (shaded ovals) in A(Ph-4-St).

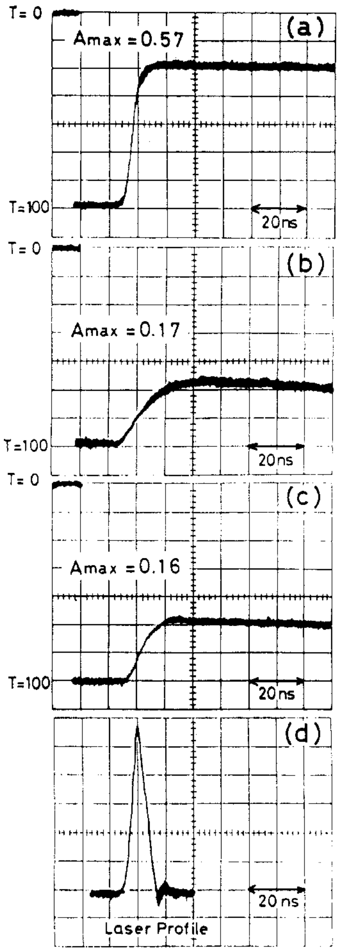


Figure 6. Rise profiles of the transient absorption due to $MV^{\bullet+}$ monitored at 602 nm in laser photolysis: (a) A(Ph-4-St), (b) A(Ph-7-LM), (c) APh-2 systems; [Phen](residue) = 0.66 mM; $[MV^{2+}]$ = 5 mM.

concentration is increased, the absorbance of the characteristic CT band[8] at about 400 nm progressively increased. As is obvious in Figure 4, this tendency is eminent for the A(Ph-7-LM) system while it is very little for the A(Ph-4-St) system. The apparent CT formation constants,[8] K_{CT}, were estimated by using the Scott equation (eq 1),[15] where

$$\frac{[MV^{2+}][Ph]_r}{\Delta A} = \frac{[MV^{2+}]}{\epsilon_{CT}} + \frac{1}{K_{CT}\epsilon_{CT}} \qquad (1)$$

$[MV^{2+}]$, $[Ph]_r$, ΔA, and ϵ_{CT} denote the molar concentrations of methylviologen and the Phen residue and the absorbance and extinction coefficient of the CT complex at 400 nm, respectively. Equation 1 is a rearrangement of the well-known Benesi–Hildebrand equation that requires an extrapolation to concentrated solutions.[15] The plots of the spectral data using eq 1 were inserted in Figure 4, and the K_{CT} values thus estimated were listed in Table I. In the case of the A(Ph-7-LM) system, both the CT complexation and fluorescence quenching were highly favorable. However, with the A(Ph-4-St) system, the CT formation was suppressed although the Phen fluorescence quenching by MV^{2+} was considerably effective; i.e., the K_{CT} value was less than half that of the APh-2 system, while the K_{SV} value was about 1 order of magnitude larger than that of the APh-2 system. These facts strongly suggest that the Phen residues in A(Ph-4-St) are successfully "compartmentalized" with the intramolecular aggregates of the pendant phenyl groups (Figure 5) such that the possibility of the Phen moieties to come into direct contact with MV^{2+} is markedly diminished, while the fluorescence from Phen can still be quenched effectively via the collisionless long-range electron transfer to MV^{2+}. These situations may be conceptually illustrated as in Figure 5.

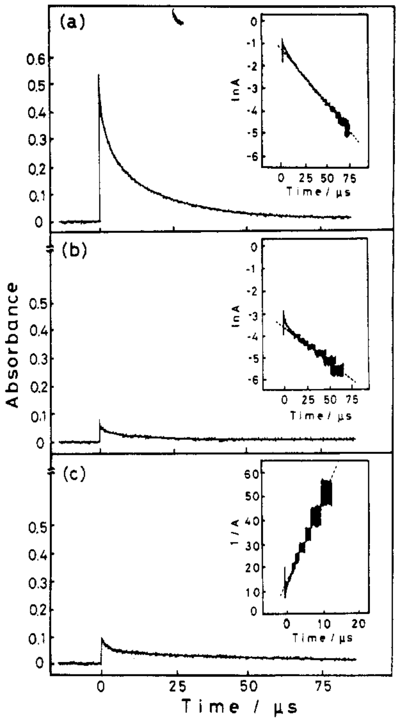


Figure 7. Transient absorption decays of $MV^{\bullet+}$ monitored at 602 nm: (a) A(Ph-4-St), (b) A(Ph-7-LM), (c) APh-2 systems; [Phen] = 0.66 mM; $[MV^{2+}]$ = 5 mM. Inserts: first-order (or second-order) plots of the decay data.

A remarkable effect of this compartmentalization of the Phen residues by the pendant phenyl groups was strongly reflected in the rise and decay profiles of the methylviologen cation radicals in laser photolysis. As presented in Figure 6a, the A(Ph-4-St) system exhibited a very rapid growth of $MV^{\bullet+}$ to give a high transient yield of $MV^{\bullet+}$. The rise process was completed within the duration time of the laser pulse, indicating that the time constant for the rise is faster than 10^8 s^{-1}. In contrast, the A(Ph-7-LM) and APh-2 systems showed slower buildups of $MV^{\bullet+}$ upon laser excitation to reach lower transient yields of $MV^{\bullet+}$. These observations are consistent with the fact that the A(Ph-4-St) system involves a more efficient fluorescence quenching and less ground-state CT complexation than in the APh-2 case (the CT complexation highly disfavors the yield of $MV^{\bullet+}$ as discussed previously[10]). The decay profiles of the viologen radicals monitored at 602 nm were exhibited in Figure 7. In the APh-2 system, the decay of $MV^{\bullet+}$ due to back electron transfer occurs mostly by a second-order process on a microsecond time scale with a rate constant of $k_b = 3 \times 10^{10}$ M^{-1} s^{-1}. However, there seems to be a fast first-order decay component in the initial stage of the decay process as is noticeable in Figure 7c.

The first-order rate constant was roughly estimated to be on the order of 10^6 s^{-1}. The A(Ph-4-St) and A(Ph-7-LM) systems also showed complicated multicomponent decay profiles in the initial stage of the $MV^{\bullet +}$ decay process (parts a and b of Figure 7). However, after several microseconds the decay profiles for both systems could well be approximated by single first-order kinetics as illustrated in Figure 7. This is indicative of the back electron transfer occurring statically with bound methylviologen cation radicals[10] because the $MV^{\bullet +}$ species have a strong tendency to be associated with the aggregates of the phenyl or lauryl residues through electrostatic as well as hydrophobic interactions. It is reasonable to consider that there is a distribution in the distance between the oxidized Phen groups and the bound $MV^{\bullet +}$ species giving rise to the complexity in the kinetics of the back reaction. An important contrast between the two systems is that the transient yield of $MV^{\bullet +}$ for the A(Ph-4-St) system is much higher than that for the A(Ph-7-LM) system. The rate constants for the back electron transfer estimated from the linear portions of the first- or second-order plot displayed in Figure 7 are listed in Table I. The rate constant for the initial decay component for the A(Ph-4-St) system was roughly estimated to be on the order of 10^5 s^{-1} which was about 1 order of magnitude smaller than that for the A(Ph-7-LM) system.

In the A(Ph-4-St) system, both the forward and backward electron transfers take place in collisionless processes as a consequence of a compartmentalization of the Phen moieties. It is important to note that in this system, the back electron transfer was slower than the forward reaction by a factor of at least 10^3. Electron-transfer theories proposed by Marcus and elaborated by others[16] predicted that in highly exothermic reactions electron-transfer rates tend to decrease with increasing exothermicity due to increasing unfavorableness in the Franck–Condon factors. Recently, evidence of the existence of this "inverted region" was experimentally demonstrated by Miller et al.[3e] and Wasielewski et al.[3g] for electron-transfer reactions in solutions. In the present case, the reaction exothermicities ($-\Delta G$) for the forward and backward electron transfer were roughly estimated to be 1.39 and 2.18 eV, respectively, using the redox potential values of $E_0(\mathrm{Phen}^{\bullet +}/\mathrm{Phen}^*) = -2.07$ V,[7] $E_0(\mathrm{Phen}^{\bullet +}/\mathrm{Phen}) = +1.5$ V,[17] and $E_0(\mathrm{MV}^{2+}/\mathrm{MV}^{\bullet +}) = -0.68$ V vs. SCE.[8] Since the back reaction is highly exothermic as compared to the forward reaction, the observed slower back reaction may be an indication of the "inverted region", with the above electron-transfer theory holding for the present case.

In the case of APh-2, the Phen groups are distributed in isolation from one another along the extended polyelectrolyte chain with which the viologen dications are ionically bound. Therefore, the encounter of the Phen sites with the bound acceptors may require a chain motion, giving rise to a dynamic nature in reaction kinetics. In a previous work,[10] we reported that in contrast to the present APh-2 case, the decay of $MV^{\bullet +}$ for the APh-9 system (the same type of copolymer as APh-2 with a Phen mole fraction of 0.09) followed predominantly a first-order rate law. In fact, we have found that the decay kinetics was strongly dependent on the Phen mole fraction in the copolymer as will be discussed in detail in the subsequent paper.[13]

An interesting observation to note is that hydrophobic aggregates of the lauryl chains and phenyl rings showed a strikingly different ability in compartmentalizing the Phen groups. As reported previously,[4] the phenyl groups covalently linked to polyanions are so closely packed in the hydrophobic aggregates that the motion of the phenyl rings are highly restricted, and thus the Phen residues may be tightly enclosed inside of the phenyl aggregates as conceptually illustrated in Figure 5. By contrast, the lauryl aggregates seem to be much looser, and therefore, they may allow methylviologen to come into contact with the Phen groups, and thereby the CT formation may strongly be favored contrary to the A(Ph-4-St) case.

From a point of view of the architecture of functionalized amphiphilic polyelectrolytes, detailed studies on the properties of the hydrophobic aggregates consisting of various types of hydrophobic groups will be an important subject of future investigations.

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Registry No. A(Ph-4-St), 108347-19-9; A(Ph-7-LM), 108347-20-2; APh-2, 81381-06-8; methylviologen, 1910-42-5.

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Thermodynamics and the Compositional Variation of Glass Transition Temperatures

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ABSTRACT: Excess properties of mixing of the thermodynamic theory for the compositional variation of glass transition temperatures are shown to be determined uniquely by the internal consistency of the general solution relations used in the theory. For the glassy state these excess properties involve solution properties and pure constituent properties of this state alone. Excess properties for the liquid state are likewise phase-consistent. From the entropy, volume, and enthalpy, general and equivalent tautological relations are derived for the compositional variation of glass transition temperatures. These reduce to separate and specific relations of approximate predictive use for in turn random, volume-additive, and athermal solutions. The formal consequences of the simultaneous validity of two or more of these different predictive theories demonstrate that such overlap would not be at all general.

Introduction

A classical thermodynamic approach I have used to provide a theory for the compositional variation of glass transition temperatures[1–9] has been said by Goldstein[10] to be incorrect. In particular, he contends that for the excess entropy of mixing of the glass the pure-constituent entropies should not all be of the glass but should be of the actual states at the conditions of interest. On the basis of this contention he claims that the predictive entropic relations I have used do not have a basis in thermodynamics per se. Their origin and success are attributed instead to the Gibbs–DiMarzio molecular theory of the glass transition,[11] a quasi-macroscopic version of which[12] can give relations identical in form with those I have used.

That an entropic relation of the thermodynamic approach does not always give exact agreement with the data is offered as support for the view that this approach is not correct. Also, the predictive entropic, volume-based, and enthalpic theories, which are particular versions of the corresponding tautologies, are compared as if these were equivalent general descriptions and as if the conditions of their consistency were an essential consequence of the thermodynamic approach. Problems are also imputed to the tautologies themselves. For example, the transition behavior of the excess volumes of mixing required by the corresponding tautology is said to be implausible.

These various claims, assertions, and interpretations are taken up below in a summary of the elements of the derivation of general thermodynamic relations for the compositional variation of glass transition temperatures and the restrictions necessary for these to be of predictive use.

The Model of the Glass Transition

Here, as previously,[1–9] the glass transition is treated formally as if it were equivalent to an Ehrenfest transition of second order.[13] In this context the only feature specific to the glass transition in the discussion below is notational. In this discussion properties of the liquid and glass are denoted by the superscripts l and g, respectively.

The aim of the thermodynamic theory to be outlined is the provision of relations between the glass transition temperature, T_g, of a single-phase solution of fixed but arbitrary composition and the glass transition temperatures, T_{g_i}, of the pure constituents from which the solution is formed. In the thermodynamic model the solution entropy, volume, and enthalpy, in turn S, V, and H, are continuous at T_g and various first derivatives of these undergo characteristic and finite discontinuities.[13] Similarly, at the T_{g_i} the variables S_i, V_i, and H_i of the separate pure constituents are continuous and various first derivatives of these undergo characteristic transition discontinuities. It is these general features of second-order transitions that are used in conjunction with the general solution relations to derive thermodynamic relations for the compositional variation of T_g.

Derivation of the Tautologies and Their Predictive Versions

The Entropic Relations. Because the nature of the excess entropies of mixing of the solution relations used in the theory is an essential point, the entropic theory is considered first. For each of the two states of the glass transition a formal connection is defined between the solution entropy and the phase-identical pure constituent properties in the same amounts, X_i, that these are present in the solution. In these solution relations[1,10]

$$S^l = \sum X_i S_i^l + \Delta S_{mix}^l \qquad (1a)$$

and

$$S^g \equiv \sum X_i S_i^g + \Delta S_{mix}^g \qquad (1b)$$

the terms ΔS_{mix}^l and ΔS_{mix}^g are the excess entropies of mixing of the liquid and glass, respectively. The sum in eq 1 and in all other relations of this paper are over all of the constituents of the solution.

The solution relations of eq 1 are formal devices through which solution and pure constituent properties of the same phase are connected. In each of these relations both the solution entropy and the pure constituent sum are specified; the single remaining term in each of these linear relations is thereby completely determined and cannot be fixed independently. Explicitly, from eq 1a the excess entropy of mixing of the liquid is the unique solution of this relation in terms of the quantities specified,

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