Macromolecules **1990,** *23,* 2598-2600

(14) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988,** *21,* 2001.
(15) Yamaoka, T.; Nishiki, M.; Koseki, K.; Koshiba, M. *Technical Papers of SPE Regional Technical Conference on Photopolymers*; 1988; p 27.
(16) Ito, H.; Willson, C. G.; Fréchet, J. M. J. *Proc. SPIE* **1987,** *771,* 24.
(17) Ito, H.; Ueda, M. *Macromolecules* **1988,** *21,* 1475.
(18) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988,** *53,* 5571.
(19) Marvel, C. S.; Overberger, C. G. *J. Am. Chem. Soc.* **1945,** *67,* 2250.
(20) Osawa, K.; Wang, K.; Kurihara, O. *Makromol. Chem.* **1965,** *83,* 100.
(21) Iwakura, Y.; Uno, K.; Nakabayashi, N.; Kijima, T. *Bull. Chem. Soc. Jpn* **1968,** *41,* 186.
(22) Yamamoto, T.; Toyoda, M.; Kitano, T.; Ito, K. *Polym. Prepr., Jpn.* **1984,** *33,* 152.
(23) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989,** *22,* 2895.
(24) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18,* 2697.
(25) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Lett. Ed.* **1979,** *17,* 759.

Notes

Effect of Microscopic Environment on Emission Quenching of Photoexcited Ruthenium Complex by Dialkylviologens

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Introduction

Photochemistry in molecular assembly systems has been extensively investigated in relation to solar energy conversion.[1-3] Some interesting effects of the microheterogeneous environments formed by molecular assemblies on photochemical reactions, especially photoinduced electron-transfer reactions, have been found.[1-4] Micellar and microemulsion systems have been studied in detail.[4-9] Kinetic behavior of a reaction between substrates solubilized in a micelle is quite different from that in a homogeneous solution.[8,10-12] In a previous paper on the quenching of a photoexcited ruthenium complex by viologens having various alkyl substituents in SDS micellar solution,[6] we found that the intramicellar electron-transfer quenching rate constants decreased with increasing alkyl chain length of the viologen quenchers from methyl to hexyl. The difference in the reactivity results from the interaction between the viologen quenchers and the micelle.

In this note, we study the quenching of a photoexcited tris(2,2′-bipyridine)ruthenium complex ($Ru(bpy)_3^{2+*}$) by viologen quenchers (C_nV^{2+}) in a polyelectrolyte (poly(styrenesulfonate)), in a polymer latex (polystyrene latex) and in a homogeneous solution (acetonitrile). It is found that the effect of hydrophobicity of the viologen quenchers (effect of alkyl chain length) on the quenching reactivity is changed drastically by the reaction environments (polyelectrolyte, polymer latex, and acetonitrile).

$$Ru(bpy)_3^{2+*} + C_nV^{2+} \rightarrow Ru(bpy)_3^{3+} + C_nV^{+} \qquad (1)$$

$$C_n\text{: } (CH_3)_2,\ (C_2H_5)_2,\ (C_4H_9)_2,\ (C_6H_{13})_2$$

Experimental Section

Poly(sodium styrenesulfonate) (PSS) was prepared by free radical polymerization of sodium *p*-styrenesulfonate with a potassium persulfate thermal initiator in water at 50 °C. The polymer was purified by ion exchanging with cation and anion exchange resins, followed by ultrafiltration. A polystyrene latex was prepared by polymerization of styrene (10 mL), methacrylic acid (1 mL), and divinylbenzene (0.1 mL) with a potassium persulfate thermal initiator in water at 70 °C. The latex solution was filtered with a 5-μm membrane to remove macroaggregates and purified by ultrafiltration (Toyo ultrafilter UK-200). The polymer latex particles were observed with a Hitachi H-300 electron microscope. The electron micrographs indicated that the latex particles were perfect spheres and almost monodisperse. The diameter of the particles was estimated to be 300 nm.

N,N′-Dialkyl-4,4′-bipyridinium halides were prepared from the reaction of 4,4′-bipyridine with the corresponding alkyl halides, and the crude products were purified by recrystallization.

All of the sample solutions were degassed by repeated freeze–pump–thaw cycles. The fluorescence intensity was measured with a Shimadzu RF 503A spectrofluorophotometer.

Results and Discussion

It is well-known that the photoexcited state of $Ru(bpy)_3^{2+}$ is redox-active and is quenched by electron-acceptor and -donor quenchers.[13,14] The excited state of $Ru(bpy)_3^{2+}$ is dynamically quenched by dialkylviologen compounds via an electron-transfer mechanism (eq 1). The relative ratios of the steady-state emission intensity of $Ru(bpy)_3^{2+*}$ in the absence (I_0) and presence (I) of viologen quencher in acetonitrile are shown in Figure 1. The redox potential of the viologens, which indicates effectiveness as an electron acceptor, was unaffected by the alkyl substituents ($E_{1/2} = -0.45$ V vs SCE).[6] It is known that the rate constants for electron-transfer quenching in homogeneous solutions are determined by the redox potentials of quenchers.[15,16] As expected from the above equivalent redox potentials of the viologens, the quench-

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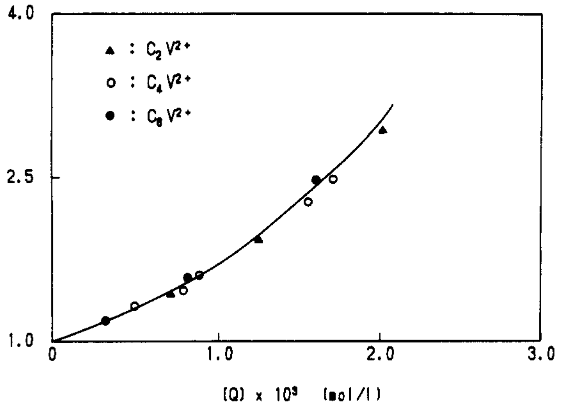

Figure 1. Stern–Volmer plots for the quenching of $Ru(bpy)_3^{2+*}$ by viologens in acetonitrile.

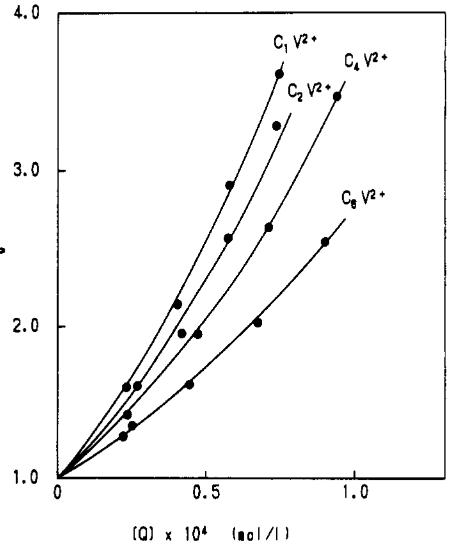

Figure 2. Stern–Volmer plots for the quenching of $Ru(bpy)_3^{2+*}$ by viologens in 0.05% poly(sodium styrenesulfonate) aqueous solution.

ing efficiency of dialkylviologens in acetonitrile did not vary with alkyl chain length. The Stern–Volmer plots of these viologen quenchers were identical. The slight curvature in Figure 1 is due to the effect of ionic strength. The equal reactivity in those viologens was also observed in the quenching of $Ru(phen)_3^{2+*}$ (phen = 1,10-phenanthroline) and $Ru(dpphen)_3^{2+*}$ (dpphen = 4,7-diphenyl-1,10-phenanthroline).[6]

Next the quenching of $Ru(bpy)_3^{2+*}$ by dialkylviologens was investigated in 0.05% poly(sodium styrenesulfonate) solution (Figure 2). It is clear that the quenching in PSS aqueous solution is more effective than that in acetonitrile. Moreover, the quenching efficiency in Stern–Volmer plots (the slopes of the plots) changed with the alkyl substituents in PSS solution but did not change in acetonitrile. The quenching efficiency decreased with increasing alkyl chain length of the viologens. Dimethylviologen was the most effective quencher. The difference in quenching efficiency caused by the alkyl substituents is attributed to the difference in hydrophobic interaction of the viologen quenchers with polyelectrolyte (PSS). Under the present conditions ($[Ru(bpy)_3^{2+}] = 2 \times 10^{-5}$ M in 0.05% PSS solution), $Ru(bpy)_3^{2+}$ is solubilized in the phase (λ_{max} is 590 nm, lifetime 0.8 μs, whereas in water λ_{max} is 585 nm, lifetime 0.6 μs) and quenched by the viologen incorporated into the polymer phase. The effective quenching in PSS solution is due to the concentration effect of the viologen in the PSS chain, where the quenching reaction is determined by the diffusion of viologen along the polymer chain as is quenching on a micelle surface. As the alkyl chain becomes longer, the viologen quencher is bound tightly to PSS due to a strong hydrophobic interaction, which results in a lowering of the quenching efficiency by suppression of the diffusion of viologen. Hydrophobic interactions in this case are an unfavorable factor for the quenching efficiency. Similar findings have been reported for the emission quenching in SDS micellar solution.[6,8]

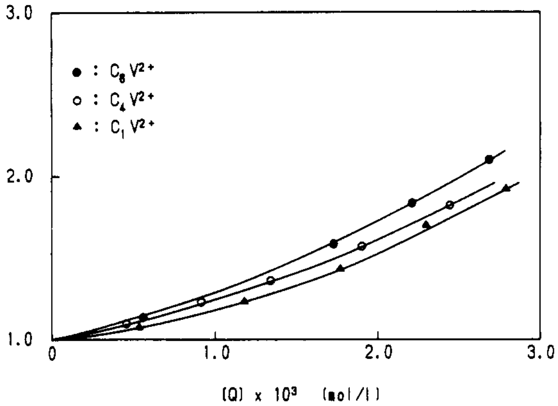

Figure 3. Stern–Volmer plots for the quenching of $Ru(bpy)_3^{2+*}$ by viologens in styrene latex aqueous solution.

Figure 3 shows Stern–Volmer plots for the quenching of $Ru(bpy)_3^{2+*}$ by dialkylviologens in a styrene latex (10 ppm) aqueous solution. Quenching in the latex solution is less effective than that in PSS solution. It leads to the conclusion that the incorporation of viologen quenchers into the latex particle is not sufficient to show effective quenching of the ruthenium complex. Moreover, the influence of the alkyl chain length is quite different from the results obtained in PSS solution. Although the variation in quenching efficiency for viologen quenchers with different alkyl chain lengths was small, the quenching efficiency of the viologen with the longer alkyl substituent (hexyl) was found to be higher than that of dimethylviologen. It is very interesting that the change in the quenching efficiency with the change in the alkyl chain length in the latex solution is reversed compared with that in PSS solution. These results could be interpreted as arising from the hydrophobic interaction. The viologen with a longer alkyl chain is incorporated to a higher extent due to hydrophobic interactions with the polymer latex, thus becoming a more effective quencher.[17] In this case, the hydrophobic interaction is a favorable factor for the quenching, since the incorporation efficiency of viologens into the latex particles determines the total quenching efficiency. On the other hand, in the PSS system, the incorporation of the viologens is sufficient for effective quenching; consequently the diffusion of viologen along the polymer chain is the rate-determining factor for the quenching. It is very interesting that the hydrophobic interaction becomes a favorable or an unfavorable factor for the quenching efficiency depending on the environments.

The present results show the importance of designing the microscopic heterogeneous environment to control the electron-transfer process. It would be necessary to accumulate the data to design molecular assembly systems for a desired functionality.

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References and Notes

(1) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 675.
(2) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982.
(3) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283.
(4) Yamaguchi, Y.; Miyashita, T.; Matsuda, M. *J. Phys. Chem.* **1981**, *85*, 1369.
(5) Thomas, J. K.; Almgren, M. *Solution Chemistry of Surfactants*; Mitall, K. L., Ed.; Plenum Press: New York, 1979; Vol. 2, p 559.
(6) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529.
(7) Miyashita, T.; Murakata, T.; Yamaguchi, Y.; Matsuda, M. *J. Phys. Chem.* **1985**, *89*, 497.
(8) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1989**, *93*, 1426.
(9) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4279.
(10) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289.
(11) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543.
(12) Dederen, J. C.; Van der Auweraer, M.; DeSchryver, F. C. *Chem. Phys. Lett.* **1979**, *68*, 451.
(13) Balzani, V.; Maggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.
(14) Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5800.
(15) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(16) Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909.
(17) Miyashita, T.; Ohsawa, M.; Matsuda, M. *Macromolecules* **1986**, *19*, 585.

Correlation between Conformational Features and the Glass Transition Temperatures for a Homologous Series of Polycarbonates

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Introduction

Attempts to predict functional properties of molecules and establish structure–property relationships via computer modeling and simulation are currently intense activities in the materials-oriented industries and the scientific community. Methodologies for computer modeling of polymer conformations and calculation of properties such as the crystalline state structure, solution configuration, etc. are well established.[1,2] Recently, from the conformational analysis of poly(methylphenylsilane) it was possible to interpret the localized hole transport behavior, as well as the molecular weight dependence of absorption maxima in the UV spectra, from a stereochemical point of view.[3]

In a recent paper,[4] a comparison of the conformational features of polycarbonates with different types of substituents at the C_α atom was presented, in terms of the rotations Φ and Ψ (see Figure 1) of contiguous phenyl groups. The small value of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and its temperature coefficient were rationalized as due to the equal energy of the conformers which lead to flat-helical and extended-helical shapes. Cyclic polycarbonates were also found to be stereochemically possible. In addition, the conformational map showed features that could account for the phenyl motion that has been detected by NMR studies.

One of the properties of polymers that is of importance is the glass transition temperature. It has long been recognized[5] that the local conformational flexibility of the chain would influence the T_g although it would not be the only determining factor. Others such as intermolecular interactions and their resultant effect on the cooperative motion of the chain segments would also contribute to the glass transition. Of course, the conformational flexibility would have an influence on the segment mobility at the local level. Tonelli[6] examined the effect of sequence distribution on the T_g for a variety of copolymers, by calculating the conformational entropy of the diad sequence and using the rotational isomeric state scheme. There have been a few recent attempts in the literature to correlate the local conformational characteristics of polymers with their glass transition temperatures.[7-9] Since in a previous paper[4] we compared the relative flexibilities of a homologous series of polycarbonates, an effort has been made here to relate the conformational flexibility of this series of polycarbonates, with different types of substituents at the C_α atom, to their glass transition temperatures. Calculations were performed for polycarbonates with the following substituents: (i) CH_3, CH_3 (2,2-diphenylpropane); (ii) H,H (diphenylmethane); (iii) H, CH_3 (1,1-diphenylethane); (iv) H, C_6H_5 (triphenylmethane); (v) CH_3, C_6H_5 (1,1,1-triphenylethane); (vi) C_6H_5, C_6H_5 (tetraphenylmethane); (vii) cyclohexyl (1,1-diphenylcyclohexane); (viii) CCl_2 (1,1-dichloro-2,2-diphenylethylene).

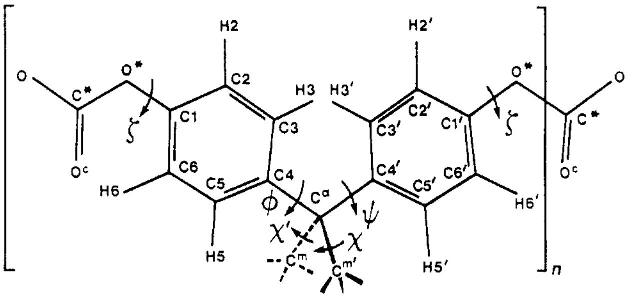

Figure 1. Schematic representation of the bisphenol A polycarbonate chain, with relevant torsional angles marked.

Calculation of Conformational Entropy

The relationship between T_g and the conformational features of the chain is explored on the basis that the T_g is related to the conformational entropy, S. Within this framework, the calculation of the conformational entropy includes only the interactions that depend on the torsional variables such as Φ, Ψ, and χ shown in Figure 1. The value of the torsion angle ζ was kept constant[4] since the substituent at the C_α atom is not expected to have an influence on this angle due to the large distance of separation. Deformation of bond angles at the C_α atom is a distinct possibility but this is ignored here. The defor-

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