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References and Notes

(1) Chin, I.-J.; Sung, C. S. P. *Macromolecules* **1984**, *17*, 2603.

(2) (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp. 146–147. (b) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10, pp 469, 475.

(3) Enns, J. B.; Gillham, J. K. *Polymer Characterization*; Craver, C. D., Ed.; Advances in Chemistry Series 203; American Chemical Society: Washington, DC, 1983.

(4) Chang, T. D.; Carr, S. H.; Brittain, J. O. *Polym. Eng. Sci.* **1982**, *22*, 1213.

(5) (a) Dusek, K.; Ilavsky, M.; Lunak, S. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 53*, 29. (b) Lunak, S.; Dusek, K. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 53*, 45.

(6) Bidstrup, S. A.; Macosko, C. W. *Proceedings of ANTEC '84, SPE* **1984**, 278.

(7) Miller, D. R.; Macosko, C. W. *Macromolecules* **1980**, *13*, 1063.

(8) The deconvolution program is based on Gaussian probability functions as described in: *Data Reduction and Error Analysis in the Physical Sciences*; Bevington, P. R., Ed.; McGraw-Hill: New York, 1969.

(9) Sung, C. S. P.; Chin, I. J.; Yu, W.-C. *Macromolecules* **1985**, *18*, 1510.

(10) Prime, R. B. *Thermal. Characterization of Polymeric Materials*; Ed. Turi, E. A., Ed.; Academic: 1981; Figure 29, p 479.

(11) Byrne, C. A.; Hagnauer, G. L.; Schneider, N. S. *Polym. Comps.* **1983**, *4*, 206.

(12) See references cited in Table 1 of: Charlesworth, J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 621.

(13) Zukas, W. X.; Schneider, N. S.; MacKnight, W. J. *Polym. Mater. Sci. Eng.* **1983**, *49*(2), 588.

(14) Bell, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 417.

(15) Morgan, R. J.; Happe, J. A.; Mones, E. T. *Proc. 28th SAMPE Symp.* **1983**, 596.

(16) Reference 10, p 443.

(17) We can calculate k_1 by expressing [b] in terms of [pp], followed by integration. However, it does not give as reliable values as those based on [ξ_a].

(18) Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. *J. Appl. Polym. Sci.* **1984**, *29*, 2481.

(19) Gupta, A.; Cizmecioglu, M.; Coulter, D.; Liang, R. H.; Yavrouian, A.; Tsay, F. D.; Moacanin, J. *J. Appl. Polym. Sci.* **1983**, *28*, 1011.

(20) Sourour, S.; Kamal, M. R. *Thermochim. Acta* **1976**, *14*, 41.

(21) Horie, K.; Hiura, H.; Souvada, M.; Mita, I.; Kambe, H. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 1357.

(22) Hagnauer, G. L.; Laliberte, B. R.; Dunn, D. A. *ACS Symp. Ser.* **1983**, *No. 221*, 231.

(23) Lippert, V. E. *Z. Elektrochem.* **1957**, *61*, 962.

(24) For a review see: Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983; Chapter 7.

(25) The ratios for A_{pt} and A_{st} are estimated from the trends of observed ratios on A_{pp}, A_{pt}, A_{ss}, and A_{tt}. The ratio for A_{ss} was determined from fraction B.

(26) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.

(27) Charlesworth, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1557.

Polymer Effects in Proton-Transfer Reactions. Poly(2-vinylquinoline)

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ABSTRACT: Emission, excitation, and absorption spectra of poly(2-vinylquinoline) and 2-methylquinoline solutions in dioxane–water mixtures have been measured as a function of the ionization degree, determined potentiometrically or spectrophotometrically. Absorption and excitation spectra give information about the ground-state equilibrium of heterocycle protonation. In the monomer analogue, the intensity of the emission coming from the protonated rings is proportional to the ground-state degree of ionization. Nevertheless, the emission coming from the heterocyclic protonated form in the polymer chain begins before the concentration of such a form would be measurable in the ground state. This is interpreted as being due to protonation of the ring following excitation as a consequence of the larger basicity of the heterocycle in the first singlet excited state when anchored in a polymer chain. The different behavior of the polymer and the monomeric model compound is interpreted in terms of the different approach to quinoline groups by solvent molecules.

Introduction

Chromophores that can undergo protonation usually have a dual emission[1,2] that is ascribed to the neutral and protonated forms. Ground-state protonation equilibrium is reflected in absorption and excitation spectra, although emission spectra are a consequence of excited-state behavior.

Ground state and excited state differ in their electronic configurations and as a consequence in their properties;[3] in particular, large basicity differences have been observed in heterocyclic systems of small molecules[2] but in only one polymer case.[4] When an aromatic heterocycle is excited, the ground-state equilibrium of protonation is perturbed

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in a manner that may produce a subsequent proton-transfer reaction. If proton affinity is smaller in the excited state, the excited-state protonated chromophore may release the proton to a solvent molecule. After decay to the ground state as the neutral form, it may recapture the proton.

In contrast, if proton affinity increases with excitation, the excited neutral form takes a proton after the necessary diffusion steps. If protons are in the immediate solvation sphere or intramolecular complexes previously exist, the diffusion step is avoided. Otherwise, the proton-transfer reaction can be diffusion controlled if the acid–base equilibrium is quickly established once the reactants are in contact.

For small molecules, when proton-transfer reactions are faster than emission, the fluorescence spectrum reflects the excited-state equilibrium population of neutral and protonated forms and therefore, only one band is observed for each pH.[5] In polymers[4] this is not so because basicity (represented by pK values) changes during the course of a titration[6] and as a consequence there is a broad range of pHs in which the degree of ionization is complete. Therefore, in polymers, to observe simultaneously the bands corresponding to neutral and protonated forms does not only have implications about the proton-transfer reaction kinetics; it is also related to the influence of repulsive interactions between ground- and excited-state protonated heterocycles.

Many other polymer effects related to energy migration, steric hindrance produced by the chain skeleton, high local chromophore concentration, etc. are expected in macromolecules that are good models for biological systems in which proton-transfer reactions play an important role.[7]

In the present work, we deal with proton-transfer reactions in the ground state and first singlet excited state of quinoline joined to a macromolecule or in a small molecule.

Experimental Section

2-Vinylquinoline was synthesized by two methods: (a) by reaction of 2-methylquinoline with 38% aqueous solution of formaldehyde in boiling triethylamine; (b) by reaction of quinoline N-oxide with vinylmagnesium chloride.

Poly(2-vinylquinoline) (P2VQ) was synthesized at 90 °C with a Ziegler–Natta catalyst ($AlEt_3/VCl_3$) under a nitrogen atmosphere and with toluene as a dispersant agent.[8] It was purified by precipitating twice in the system benzene/n-hexane as solvent/precipitant and dried under vacuum. Molecular weight determined by light scattering in chloroform was $M_w = 7.33 \times 10^5$. Crystallinity was 57%, determined in a Philips 1100 X-ray generator with Cu Kα radiation. 2-Methylquinoline (2MQ) was from Ferosa. It was distilled under vacuum just prior use.

Organic solvents were RPE products from Carlo Erba. Water was distilled and purified in a Milli-Q system from Millipore. Solvents for fluorimetry were found to be transparent and clear in the spectral region employed. Standard HCl solutions from Carlo Erba were checked by potentiometric titration with anhydrous sodium carbonate.

pH measurements were performed in a pH meter from Radiometer. Corrections for the liquid junction potential[9] were applied for each dioxane–water composition and HCl concentration.

Absorption spectra were measured in a Perkin-Elmer 124 spectrophotometer with cells of 10- or 2-mm optical path length.

Fluorescence measurements were performed in a Perkin-Elmer LS-3 fluorometer. Spectra were uncorrected. Nitrogen bubbling decreases the emission of the neutral and protonated forms by less than 10% and so aerated solutions were employed.

In all cases polymer concentration was kept below 5×10^{-4} M (OD < 1) in order to avoid autoabsorption in fluorescence spectra and aggregation problems. 2MQ was used at the same concentrations.

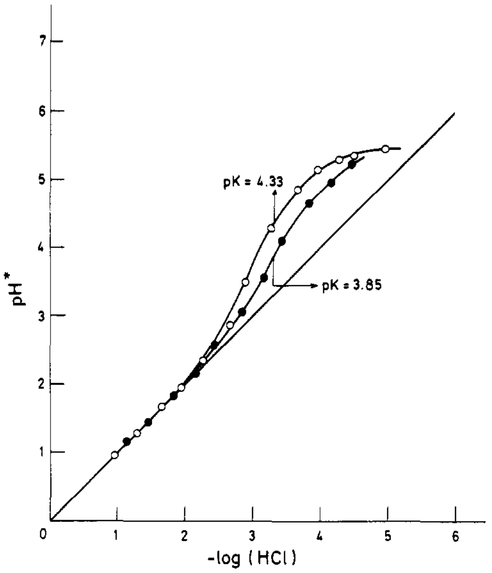

Figure 1. Potentiometric titration of 2MQ in two dioxane–water mixtures of different dioxane volume fraction: (○) $\phi_{diox} = 0.500$; (●) $\phi_{diox} = 0.667$.

Table I
pK Values in the Ground (pK) and First Single Excited State (pK*) for 2MQ and P2VQ in Dioxane-Water Solutions of Different Dioxane Volume Fraction (ϕ_{diox}) at Room Temperature

		P2VQ	
ϕ_{diox}	2MQ	$\alpha,\alpha^* = 0.1$	$\alpha,\alpha^* = 0.5$
0.500	pK = pK* = 4.33	pK = 1.33 pK* = ...	pK = 1.60 pK* = ...
0.667	pK = pK* = 3.85	pK = 2.60 pK* = 3.80	pK = 2.85 pK* = 4.40

Results and Discussion

Ground-State Ionic Equilibrium. Potentiometric determination of the ionization degree (α) and the apparent pK_a in a polybase partially protonated by HCl is made through the expressions

$$\alpha = ([\mathrm{HCl}] - [\mathrm{H}^+])/[\mathrm{P2VQ}]_{tot} \tag{1}$$

$$\mathrm{p}K_a = \mathrm{pH} + \log [\alpha/(1 - \alpha)] \tag{2}$$

where $[\mathrm{P2VQ}]_{tot}$ represents the polymer concentration.

But pH measurement does not allow the estimation of α and pK_a of dilute (5×10^{-4} M) P2VQ solutions in dioxane–water mixtures because pH*, i.e., pH corrected for the liquid junction potential, is approximately equal to –log [HCl].

Nevertheless, that is not the case for the monomer analogue 2-methylquinoline, as can be seen in Figure 1. As expected, when the water content increases and therefore the solvent dielectric constant increases, pK_a increases and heterocycle ground-state protonation becomes easier. In pure water at 20 °C, pK_a = 5.83,[10] in accordance with the extrapolated value from our results in water–dioxane mixtures (Table I).

In the same solvent, P2VQ is comparatively much less basic than 2MQ, according to the potentiometric results. It is a general result in polybases and several arguments have been claimed to explain it.[11,12] They consider the influence of the polymer skeleton through its hydrophobicity and giving place to a low local dielectric constant.[11,12] Preferential sorption of the low dielectric constant solvent must also be considered in solvent mixtures.

P2VQ excitation spectra (Figure 2) show two partially overlapping bands. The relative intensities and peak

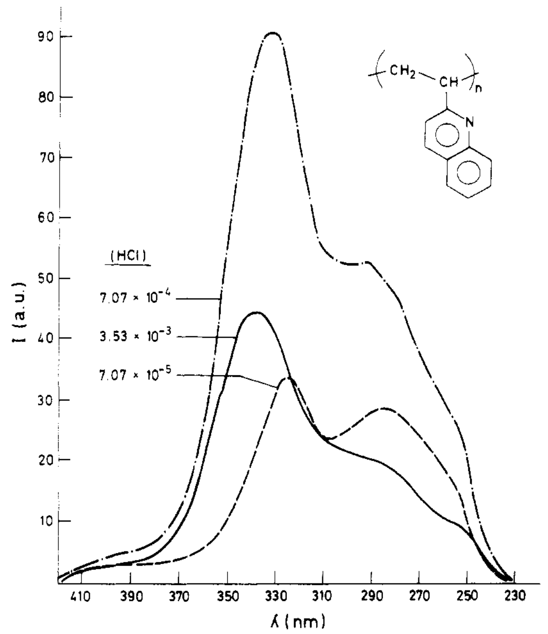

Figure 2. Excitation spectra of P2VQ in dioxane–water solutions (ϕ_{diox} = 0.667) at different HCl concentrations. The emission wavelength λ_{em} = 460 nm.

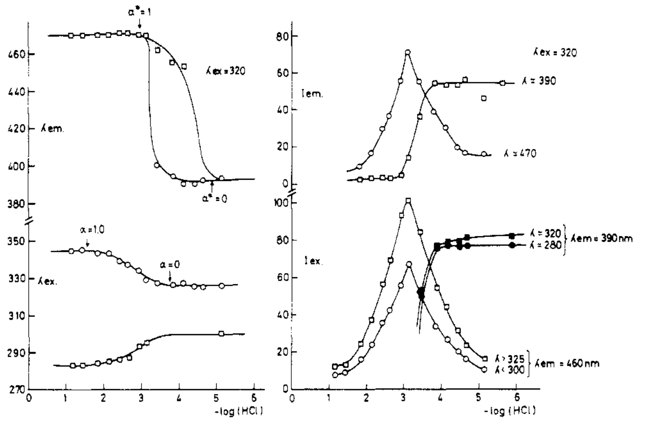

Figure 3. P2VQ emission and excitation characteristics (maximum intensity (I) and wavelength (λ)) in a dioxane–water solution (ϕ_{diox} = 0.667) as a function of HCl concentration.

wavelengths change with the HCl concentration as shown in the lower part of Figure 3 for mixtures containing 66.7% dioxane in volume fraction.

P2VQ and 2MQ absorption spectra are essentially the same. Figure 4 shows the absorption spectra of 2MQ in dioxane–water at several HCl concentrations. They show, as the excitation spectra, two bands whose relative intensity changes with the degree of ionization, but in the absorption spectra there are no shifts of the peak wavelengths as in excitation.

Although a precise potentiometric determination of α is impossible for P2VQ as mentioned before, it is possible to estimate the ground-state degree of protonation by means of absorption and excitation spectra. Intermediate values of α can be interpolated by assuming that the plateaus of λ_{ex} vs. −log [HCl] (Figure 3) at low and high [HCl] correspond to zero and complete ionization. About the same results are obtained by using the dependence of the optical density on −log [HCl]. Table I summarizes the P2VQ pK values calculated with expression 1 and 2 at two α values and compares them with the pK for 2MQ.

It must be mentioned here that the P2VQ sample used is highly isotactic, and tacticity influences in polymer basicity have been previously found[13] for another polybase: poly(2-vinylpyridine).

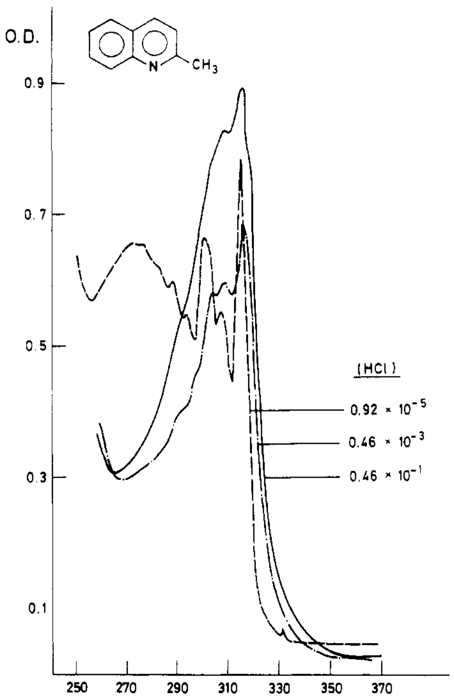

Figure 4. Absorption spectra of 2MQ in dioxane–water solutions (ϕ_{diox} = 0.667) at different HCl concentrations.

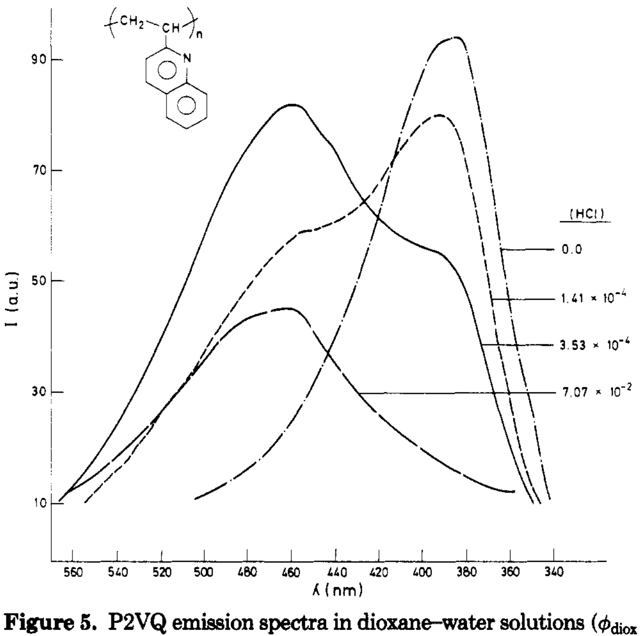

Figure 5. P2VQ emission spectra in dioxane–water solutions (ϕ_{diox} = 0.667) at different HCl concentrations. The excitation wavelength λ_{ex} = 320 nm.

Excited-State Behavior. Excited-state behavior is reflected in the emission properties. P2VQ fluorescence spectra in dioxane–water solutions of 66.7% dioxane volume fraction containing different concentrations of HCl are shown in Figure 5. They show two bands that coexist in a certain range of HCl concentrations. The peak around 390 nm that appears at lower HCl concentrations is ascribed to rings that are neutral in the excited state. At larger HCl concentrations a new broader band appears around 470 nm and is ascribed to excited-state protonated rings (Table II). Therefore, the transition from 390 to 470 nm for λ_{em} (Figure 3) allows estimation of the ionization

Table II
Spectral Characteristics of the Neutral (N) and Protonated (P) Forms of 2MQ and P2VQ in Dioxane–Water Mixtures: Emission (λ_{em}), Absorption (λ_{ab}), and Excitation (λ_{ex}) Wavelengths and Stokes Shifts (S)

	λ_{em}, nm	λ_{ab}, nm	λ_{ex}, nm	S, cm^{-1}
2MQ → N	340	314	293	4720
2MQ → P	405	314	337	4980
P2VA → N	390	319	326	5030
P2VQ → P	470	313	345	7710

degree in the excited state (α^*) as a function of the HCl concentration.

Total ionization of the first singlet excited state of heterocycles anchored in the polymer chain occurs at pH between 4.75 and 3.25 when $\phi_{diox} = 0.667$ whereas ionization of the ground state under the same conditions requires larger HCl concentrations with pHs ranging from 3.75 to 1.70.

Analogous behavior is observed when the dioxane volume fraction in the solvent mixture is 50%. In this case ground-state protonation occurs between 3.25 and 0.50 pH, and excited-state ionization is complete at pH 3.25. Solubility problems prevent determination of the pH at which excited-state ionization begins, and therefore pK^* cannot be calculated for this ϕ_{diox}.

Table I summarizes pK and pK^* values for P2VQ in two dioxane–water solutions and at two ionization degrees. It is clear from these results that quinoline heterocycles are much more basic in the excited state than in the ground state when they form part of the homopolymer P2VQ. As a consequence, when only neutral rings are present in the ground-state ionization equilibrium, immediately after the absorption of light that situation is no longer in equilibrium since the chromophore basicity has suddenly increased. To restore the protonation equilibrium, the heterocycle in the excited state takes a proton from the surrounding solvation atmosphere. Once protonated, it decays to the ground state. Then it releases the proton again to the first solvation shell.

Nevertheless, basicity of quinoline in 2MQ is the same in the ground state and in the first singlet excited state, as we will see now. 2MQ emission in dioxane–water solutions, at very low HCl concentration, shows only one very weak band around 340 nm. It corresponds to the neutral form. Intersystem crossing, typical of heterocycles, may explain the low fluorescence quantum yield. When the HCl concentration increases, a new band at 405 nm appears with intensity comparable to the P2VQ emission (Table II). The intensity of this last band, ascribed to protonated 2MQ in the first singlet excited state, is proportional to the ground-state ionization degree (Figure 6), and it must be interpreted as if $\alpha^* = \alpha$ and therefore pK = pK^*. That is to say the 2MQ basicity is the same in the ground and excited states, and the ionization equilibrium is not perturbed by excitation to the first singlet excited state at room temperature.

At very large [HCl]/[chromophore] ratios, when there are five molecules of HCl per 2MQ molecule and the ionization degree is 90%, fluorescence is quenched when the HCl concentration increases. The same phenomenon occurs in the polymer, but at lower HCl concentrations (Figure 3), when there are only 2.6 HCl molecules per heterocycle joined to the polymer chain and the ionization degree is about 20%. Above that HCl concentration, the P2VQ fluorescence intensity decreases progressively and disappears at pH around 1. Fluorescence quenching by counterions has previously been observed for poly(2-vinylpyridine) and it was ascribed to the formation of a charge-transfer complex,[4] typical of heterocyclic systems.[14] The formation of such charge-transfer complexes is related to counterion condensation on the protonated ring.[12,14] As expected,[4] upon addition of Na_2SO_4, the quenching efficiency of chloride counterions decreases.

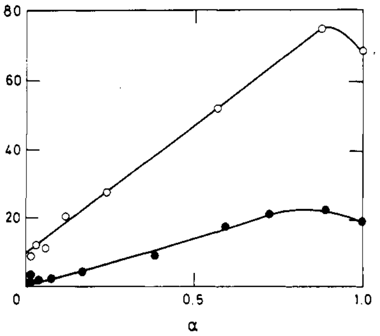

Figure 6. Emission intensity at 410 nm of 2MQ solutions in dioxane–water mixtures of different dioxane volume fraction: (○) $\phi_{diox} = 0.500$; (●) $\phi_{diox} = 0.667$.

Polymer Effects. Differences between P2VQ behavior and that of its monomeric model compound 2MQ are attributed to phenomena specific to macromolecular systems, which we call polymer effects.

Changes in basicity accompanying excitation are the consequence of chromophore conformational changes.[3] In 2MQ basicity is the same in the ground state and in the first singlet excited state, but there is experimental evidence of quinoline conformational changes produced by electronic excitation in that compound. Such evidence comes from Stokes shifts of the neutral and protonated forms of quinoline.

The Stokes shift S is given by

$$S = 10^7/\lambda_{ex} - 10^7/\lambda_{em} \tag{3}$$

where λ_{ex} and λ_{em} are the excitation and emission wavelengths (in nm), respectively. It measures the difference in energy between Franck–Condon and equilibrium states and depends on the degree of relaxation of the solvent molecules produced in the chromophore solvation shell by conformational changes in the molecule.[2] Table II summarizes S values for 2MQ an P2VQ. In all cases, the stabilization of the excited state by redistribution of solvent molecules is quite strong. Conformational changes occur in both compounds, although they are more drastic in the polymer case.

If 2MQ suffers photoinduced conformational changes but its basicity does not change with excitation, it could mean that proton-transfer reactions occur from Franck–Condon excited states and therefore they compete with solvent relaxation. This interpretation is in accordance with experimental and calculated photoinduced pK changes.

The Förster cycle[1] allows calculation of such ΔpK by means of the expression

$$\Delta pK = pK^* - pK = (h\nu_Q - h\nu_{QH})/2.3RT \tag{4}$$

where ν_Q and ν_{QH} are the frequencies of the electronic transitions in the neutral and protonated forms and h is the Planck constant. In systems with large Stokes shifts, two choices can be made for ν_Q and ν_{QH}: those from emission spectra and those from absorption spectra. Frequencies from emission spectra involve the equilibrium excited states, and frequencies from absorption spectra involve the Franck–Condon excited states.

Table III summarizes ΔpK calculated values with emission and excitation data of Table II and also with

Table III
Photoinduced pK Increase ($\Delta pK = pK^* - pK$) for Quinoline in 2MQ and P2VQ

	ΔpK_{exptl}[a]	ΔpK_{em}[b]	ΔpK_{ex}[b]	ΔpK_{av}[c]
2MQ	0	9.9	9.3	9.7
P2VQ	1.4	9.2	3.5	7.1

[a] Experimental results. [b] Calculated by the Förster cycle using emission (ΔpK_{em}) and excitation (ΔpK_{ex}) data. [c] Calculated by the Förster cycle using the average of excitation and emission wavelengths.

averages[1] of those two values. The closest approach to experimental results in the P2VQ case corresponds to excitation data, in agreement with previous arguments about the electronic excited state involved in proton-transfer reactions, the Franck–Condon level. For 2MQ, ΔpK calculated values overestimate the experimental result. Perhaps solvent relaxation in this case is faster than the proton-transfer reaction and the equilibrium excited state is not able to react.

Differences in ground-state basicity and excited-state behavior for the polymer and the monomer analogue suggest that the chromophore approach by solvent molecules is very different in the two cases. Chromophore packing in the polymer chain and steric hindrance of the backbone, which is especially important in position 2,[15] make the quinoline–solvent interaction difficult. As a consequence, local dielectric constant and ground-state basicity are different for the polymer and the monomer analogue, and that influences too the rate of proton-transfer reaction with respect to the rate of solvation atmosphere relaxation.

Conclusions

Several polymer effects have been observed from comparison of the ionization equilibria of P2VQ and its monomer analogue 2MQ. (i) Ground-state basicity is much smaller for the polymer than for the small compound. (ii) P2VQ suffers proton-transfer reactions in the first singlet excited state and 2MQ does not. (iii) Charge-transfer complexes with counterions quench the emission at lower acid concentrations for the polymer than for 2MQ.

These effects are explained by the following arguments: (i) Excitation produces chromophore conformational changes both in the polymer and in the monomer analogue. (ii) Proton-transfer reactions occur from Franck–Condon excited states and compete with solvent relaxation, both in the polymer and in the monomer analogue. (iii) Solvent molecule approach to quinoline is different in 2MQ and P2VQ. As a consequence, proton-transfer reactions are faster than solvent relaxation processes in the polymer case, but the opposite is true for 2MQ. This also explains the ground-state behavior of both compounds.

These interpretations are in agreement with Stokes shifts and calculated pK values.

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Registry No. 2MQ, 91-63-4; P2VQ, 33638-30-1.

References and Notes

(1) Huppert, D.; Gutman, M.; Kaufmann, K. J. In *Adv. Chem. Phys.* **1981**, *47*(2), 643.
(2) Schulman, S. G. In *Physical Properties of Heterocyclic Compounds*; Katritzky, A. R., Ed.; Academic: New York, 1974; Vol. VI, p 147.
(3) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.
(4) Piérola, I. F.; Turro, N. J.; Kuo, P. L. *Macromolecules* **1985**, *18*, 508.
(5) Donckt, E. V. *Prog. React. Kinet.* **1970**, *5*, 273.
(6) Morawetz, H. *Macromolecules in Solution*; Wiley-Interscience: New York, 1975.
(7) Caldin, E.; Gold, V. *Proton Transfer Reactions*; Chapman and Hall: London, 1975.
(8) Alberola, A.; Benito, Y.; Rodríguez, J. G.; Esteban, S.; Gómez-Antón, M. R. *Eur. Polym. J.* **1986**, *22*, 323.
(9) Bates, R. G. *Determination of the pH:Theory and Practice*, 2nd ed.; Wiley: New York, 1973.
(10) Barton, D.; Ollis, D. *Comprehensive Organic Chemistry*; Pergamon: New York, 1979; Vol. 4, p 166.
(11) Katchalsky, A.; Mazur, J.; Spitnik, P. *J. Polym. Sci.* **1955**, *23*, 513.
(12) Kirsh, Y. E.; Komarova, O. P.; Loukukin, G. M. *Eur. Polym. J.* **1973**, *9*, 1405.
(13) Kitajima, H.; Yamashita, T. *Polym. J. (Tokyo)* **1973**, *4*, 262.
(14) Kosower, N. M.; Klinedinst, P. E. *J. Am. Chem. Soc.* **1956**, *78*, 3493.
(15) Nolleben, J.; Testa, A. C. *J. Photochem.* **1982**, *19*, 267.

Photophysics of Polystyrene. 1. A Monte Carlo Study

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ABSTRACT: Investigations have been carried out on intramolecular excimer formation, quantum yields, times of fluorescence decay, and energy migration (EM) in polystyrene (PS) as a function of molecular weight by using the Monte Carlo method. Mechanisms (resonance and exchange) that may be responsible for PS luminescence have been discussed, and it has been shown that the exchange (Dexter's) mechanism is more appropriate in the description of the EM process. The observed differences in quantum yield obtained by experiment and by Monte Carlo simulation have been explained by PS chain dynamics, which are not taken into account in the simulation. The following photophysical parameters of PS have been determined: concentration of excimer-forming sites, average time of energy hop between chromophoric groups, average number of energy hops, and average square of the angle between electronic transition moments in phenyl groups.

I. Introduction

Investigations of migration and transfer of electronic excitation energy have been conducted on a number of substances, which, owing to the distribution of luminescent molecules, may be divided into homogeneous and nonhomogeneous substances.

The study of luminescence processes in nonhomogeneous systems, which include, among others, biological cells,

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