as depicted in Scheme I. Branch a of Scheme I represents an attack of a phenoxyl radical with high selectivity at the para position of a phenoxide ion, while branch b represents the attack of a phenoxide ion at the ortho position of a phenoxyl radical. It is not necessary to postulate high selectivity for the latter reaction since attack at the para position would also give products in agreement with experimental observation. The selectivity of branch a is necessary to explain the apparent absence of 1,2-enchainment. It is envisaged that propagation occurs rapidly by branches a and b simultaneously during the lifetime of a radical.

Given the differences between generation of phenoxide and phenoxyl radicals in aqueous alkali and in a copper complex in a low dielectric organic solvent (or even in a solid copper complex), it is quite remarkable that the polymer structures are so similar.

Experimental Section

The synthesis of poly(dibromophenylene oxide) by decomposition of copper tribromophenoxide in acetonitrile has been described previously.[1] The free radical polymerization of tribromophenoxide was effected by a modification of a procedure reported by Stamatoff.[5] To a solution of tribromophenol (3.3 g) in deaerated distilled water (100 mL) containing sodium hydroxide (0.4 g) was added potassium persulfate (0.1 g). The solution was stirred for 12 h and a further aliquot of initiator was added (0.1 g). After a further 12 h at room temperature the reaction mixture was heated to 80 °C for 1 h and then filtered. The resulting polymer was dried, redissolved in a few milliliters of toluene, and reprecipitated in a large excess of methanol containing a small amount of hydrazine. The resulting white polymer was filtered, washed with methanol, and dried in a vacuum oven overnight at 100 °C; yield 1.8 g (75%).

The ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ (ca. 20% w/v) with a Varian XL-200 spectrometer. Operating conditions were the same as described previously.[1]

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References and Notes

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(3) Although it is generally assumed that the electron-deficient radical attacks the high electron density regions of the electron-rich phenoxide, there appears to be no good reason for excluding the converse process, i.e., attack of the nucleophilic phenoxide at the low electron density regions of the radical.
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Comment on "Interpretation of the Excimer Kinetics of Poly(*N*-vinylcarbazole) and 1,3-Dicarbazolylpropane in Dilute Solutions" (*Macromolecules* 1981, *14*, 405)

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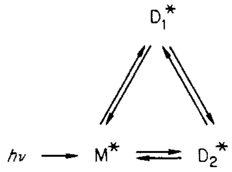
In a recent paper[1] time-resolved fluorescence measurements were reported for poly(*N*-vinylcarbazole) in solution. Results were interpreted in terms of a kinetic scheme, Scheme I, where M* represents an uncomplexed monomer carbazole chromophore, D_1* a high-energy excimer site emitting at λ_{max} 370 nm, and D_2* a sandwich excimer emitting at λ_{max} 420 nm. In this scheme it will be noted that only one high-energy excimer, D_1*, is postulated and that the low-energy D_2* is populated through both the high-energy excimer and directly from the monomer, with the latter being the favored route. Although structural difference between samples of poly(*N*-vinylcarbazole) prepared under nonidentical conditions may preclude exact comparison of fluorescence decay data, in the light of our own experiments on these systems, we wish to make the following comments upon this interpretation.

Scheme I



(a) The attributing of the component with a 60-ps decay as due to monomer M* in Scheme I is in agreement with the work of Ghiggino et al.[2] In our experiments we were not able to resolve this component.

(b) In the experiments of Ng and Guillet,[1] the analysis of the fluorescence decay recorded at 420 nm revealed a component with a lifetime of 60 ps with a negative preexponential factor, suggesting that the growth of the low-energy "sandwich" excimer was due to the decay of the monomeric species. This observation was said to explain the slow growing in of the low-energy emission band observed in time-resolved emission spectra reported previously.[3,5,6] Examination of these, however, reveals that little sandwich excimer fluorescence may be observed during the first few nanoseconds following excitation and, consequently, the main route to the formation of the sandwich excimer must involve a rise time considerably longer than the 60 ps suggested.[1] Indeed nanosecond rise times have already been reported by Tagawa et al.[4] (2 ns) and Roberts et al.[3] (2.6 ns). This rise time corresponds to the decay of a species emitting at 370 nm and is assigned to either a "relaxed monomeric" moiety[4] or a *third* excimer.[3] The conclusion reached by us was that the low-energy excimer was excited principally via this high-energy species and not from the directly excited monomer.

(c) It is necessary to consider why the rise times of 2[4] or 2.6 ns[3] clearly seen by us and other workers were not seen by Ng and Guillet.[1] We believe the choice of wavelength used to monitor the sandwich excimer fluorescence was unfortunate. At this wavelength the high-energy excimer also emits, and thus measured decays will not correspond purely to those of the sandwich excimer. The lifetime observed by Ng and Guillet in the range 2.3–3.0 ns has a small positive preexponential factor. We believe this is due to simultaneous observation of the *decay* of the component at 380 nm and the *rise* of the 420-nm component, leading to almost complete cancellation of *A* factors. In experiments performed in our laboratory, in order to measure decay parameters which were independent of the fluorescence wavelength, thus corresponding to the emission from solely the low-energy excimer, it was necessary to observe at wavelengths longer than 450 nm.

(d) We accept that the observation by Ng and Guillet of a negative preexponential factor for the 60-ps decay time in the emission at 420 nm indicates that the low-energy excimer *is* populated directly from the excited monomer, although in view of the above discussion we maintain this to be a minor process.

(e) Ng and Guillet presented no evidence for a second high-energy emitting species as observed by Roberts et al.[3]

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and Tagawa et al.,[4] although this would have necessitated fluorescence decay analysis using four exponential terms with eight independently varying parameters, imposing severe demands upon the quality of experimental data and analysis procedure.

In conclusion, while we agree that a scheme of the type shown in Scheme I is necessary to explain the observed fluorescence from PVCz, we do not accept that the evidence presented by Ng and Guillet is sufficient to support their contention that the main route populating D_2* is directly through the monomer. Moreover, we think the case for there being two independent high-energy excimer species emitting at 370 nm is well established.

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Catalysis by Polyelectrolytes Whose Monomeric Units Behave Independently: Effect of a Poly(amido amine) on the Ionization Rate of Ethyl Nitroacetate

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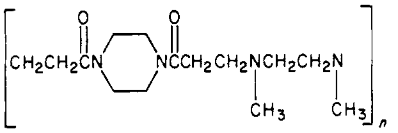
It has been recently discovered[1] that a new family of water-soluble tertiary amino polymers of regular structure, poly(amido amines), behaves toward protonation and complex formation in a way that can be considered unusual in the domain of macromolecules. As a matter of fact the basicities of the tertiary amino groups present in the repeating units of poly(amido amines) are not affected by the degree of protonation of the remainder of the macromolecule,[1-5] while the opposite is true in the case of most polyelectrolytes described[6] so far. As a consequence, poly(amido amines) exhibit as many basicity constants as aminic nitrogens in their repeating units, and these constants can be determined with a high degree of accuracy.[1-5]

This prompted us to investigate the properties of these polymers also in other domains of chemistry. In particular, we thought it interesting to study the use of poly(amido amines) as catalysts and to compare their behavior with that of nonmacromolecular molecules.

This paper reports on the first results obtained by measuring the ionization rates of ethyl nitroacetate in aqueous solution catalyzed by a poly(amido amine) (B) having a number-average molecular weight 10 300 derived from the polyaddition of *N,N'*-dimethylethylenediamine to 1,4-bis(acryloyl)piperazine:[7]



B

This study has been carried out by the "stopped-flow" technique.

The rate of ionization of ethyl nitroacetate was followed by directly observing the formation of the anion, which strongly absorbs at 300 nm. All kinetic measurements were carried out at 25 °C and 0.1 M ionic strength, adjusted by $NaClO_4$. Individual rate constants were the average of 3–7 sets, each of which was the result of at least 8 accumulations. These rate constants were reproducible to within 5%.

The ionization of ethyl nitroacetate (SH) in aqueous solution (eq 1) has been chosen as a model reaction for our

$$\mathrm{SH} + \mathrm{B} \underset{k_{\mathrm{BH^+}}}{\overset{k_\mathrm{B}}{\rightleftharpoons}} \mathrm{S^-} + \mathrm{BH^+} \tag{1}$$

SH = ethyl nitroacetate

studies on the catalytic activity of poly(amido amine) (B) because it offers several advantages. First of all, the formation of the conjugate base can be conveniently followed by observing its strong absorption at 300 nm. Furthermore, the quantitative relationship between catalytic power (log k) and basic strength of the catalyst ($\mathrm{p}K_\mathrm{a}$) has been firmly established for several nonmacromolecular bases having a wide range of $\mathrm{p}K_\mathrm{a}$ (over 10 orders of magnitude).[9] Recently, the same reaction has been used to investigate the catalytic behavior of some macrobicyclic ligands and to detect and interpret their derivations from Brønsted relationship.[9]

Experimental Section

Materials. Commercial ethyl nitroacetate (Aldrich) was distilled under reduced pressure just before us. Poly(amido amine) (B) was prepared as previously described.[7] Its molecular weight was determined osmometrically. $NaClO_4$ (AnalaR, BDH) was used without further purification.

Apparatus and Methods. A Jasco J-500A stopped-flow apparatus equipped with a DP-500 on-line data processor was used. The stopped-flow apparatus was calibrated by measuring known rates of reduction of $K_3Fe(CN)_6$ by L-ascorbic acid at 420 nm at 25 °C in several buffered aqueous solutions.[8] Rate constants were in agreement (within 2%) with literature values.

The reaction conditions were such that the reverse reaction of equilibrium 1 could be ignored, the $\mathrm{p}K_\mathrm{a}$ of SH being 5.80 and the $\mathrm{p}K_\mathrm{a}$ of B being 8.09.[2] The concentration of the base was considerably higher ($2 \times 10^{-1} \geq [\mathrm{B}] \geq 48 \times 10^{-4}$) than that of the substrate ($2.0 \times 10^{-5} \leq [\mathrm{SH}] \leq 6.4 \times 10^{-5}$). Under these conditions the appearance of S^- follows pseudo-first-order kinetics:

$$+\mathrm{d}[\mathrm{S^-}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{S^-}]$$

where

$$k_{\mathrm{obsd}} = k_{\mathrm{OH}}[\mathrm{OH^-}] + k_\mathrm{B}[\mathrm{B}]$$

Results and Discussion

The results of our measurements are reported in Table I, together with some experimental details. It may be observed that the rate constant values steadily increase with increasing catalyst concentration at constant pH. Second-order rate constants are independent of the $[\mathrm{B}]/[\mathrm{BH^+}]$ ratio. This means that only the unprotonated species acts as a catalyst, while the contribution of BH^+, which also, in principle, might show catalytic activity, is negligible. This could be reasonably expected by consid-

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