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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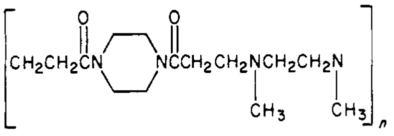
It has been recently discovered[1] that a new family of water-soluble tertiary amino polymers of regular structure, poly(amido amines), behaves toward protonation and complex formation in a way that can be considered unusual in the domain of macromolecules. As a matter of fact the basicities of the tertiary 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

$$SH + B \underset{k_{BH^+}}{\overset{k_B}{\rightleftharpoons}} S^- + BH^+ \qquad (1)$$

$$SH = \text{ethyl nitroacetate}$$

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 (pK_a) has been firmly established for several nonmacromolecular bases having a wide range of pK_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 pK_a of SH being 5.80 and the pK_a of B being 8.09.[2] The concentration of the base was considerably higher ($2 \times 10^{-1} \geq [B] \geq 48 \times 10^{-4}$) than that of the substrate ($2.0 \times 10^{-5} \leq [SH] \leq 6.4 \times 10^{-5}$). Under these conditions the appearance of S^- follows pseudo-first-order kinetics:

$$+d[S^-]/dt = k_{obsd}[S^-]$$

where

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

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 $[B]/[BH^+]$ 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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Table I
Rates of Ionization of Ethyl Nitroacetate Catalyzed by Poly(amido amine) B in Aqueous Solutions at 25 °C (Ionic Strength = 0.1 M)

I. Buffer Ratio $[B]/[BH^+] = 1$

$10^4[B]$	2.00	4.00	6.40	10.0
k_{obsd}/s^{-1}	1.39	3.10	4.94	8.25
$k_{calcd}{}^a/s^{-1}$	1.61	3.21	5.14	8.03

II. Buffer Ratio $[B]/[BH^+] = 2$

$10^4[B]$	8.00	16.0	24.0	32.0	48.0
k_{obsd}/s^{-1}	9.60	15.7	22.3	30.3	39.1
$k_{calcd}{}^b/s^{-1}$	9.58	16.2	22.7	29.3	42.5

[a] Calculated from the equation $k_{calcd} = 8.03 \times 10^3[B]$. [b] Calculated from the equation $k_{calcd} = 3.0 + 8.23 \times 10^3[B]$.

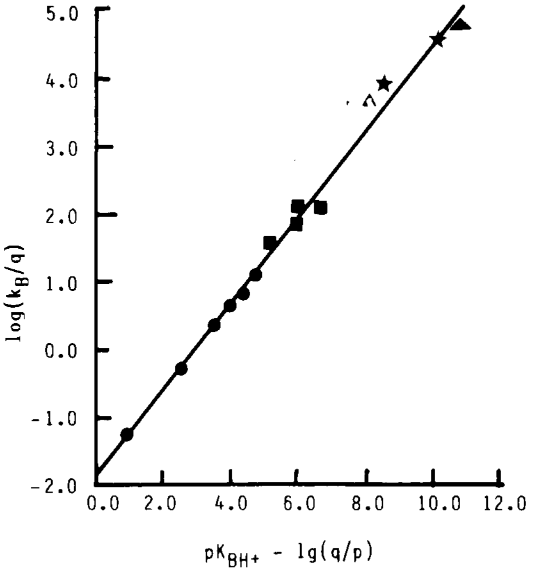

Figure 1. Dependence of the rate of ionization of ethyl nitroacetate upon the strength of the reacting base: (▲) triethylamine; (★) phenoxide ions; (■) pyridines; (●) carboxylate anions;[9] (△) poly(amido amine) B. p and q are statistical correction terms allowing for the number of dissociable protons (p) and the number of equivalent points at which a proton can be attached (q) (see also ref 10).

ering the low basicity of BH^+ as compared with that of B: $pK_a(BH_2{}^+) = 4.54$.[2] It may also be pointed out that a smaller contribution by OH^- is detectable only at buffer ratio $[B]/[BH^+] = 2$, as expected from the known value of k_{OH}.[9]

From the above results it may be concluded that the poly(amido amine) studied in the present work acts as catalyst in the ionization reaction of ethyl nitroacetate in a way predictable by the Brøsted equation established for "normal" bases (see Figure 1) (average $k_B = 8.13 \times 10^3$ mol^{-1} dm^3 s^{-1}).

This further confirms that the repeating units of this polymer behave independently and that no significant effects due to macromolecularity are present. To our knowledge, this is first instance in which the catalytic power of a synthetic polymer can be quantitatively related to a thermodynamic quantity of the same polymer, namely, its basicity constant, which, owing to the peculiar nature of poly(amido amines), had been accurately determined.[2]

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Calculation of Spinodals for Quasi-Binary Polymer Systems

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The spinodal is the locus of temperature–concentration pairs for which the Gibbs free energy of mixing has an inflection point.[1] Physically, the spinodal determines limits of metastability of the system. In polymer systems, the free energy function is sensitive to polydispersity.[2] Therefore, a convenient method for locating spinodals, for example, the pulse-induced critical scattering method,[3] could provide a source of information about the systems, including that of the polydispersity of the polymers involved. The free energy function ΔG_{mix} itself should then serve as a means for calibration. For polymers consisting of, say, N components differing in length, the spinodal condition is given by the Gibbs equation[1]

$$\det \{\partial^2 \Delta G_{mix}/\partial\phi_i \partial\phi_j;\ i, j = 1, 2, ..., N\} = 0 \tag{1}$$

where ϕ's are the concentrations of the components, conveniently expressed as the volume fractions.

Equation 1 becomes more and more difficult to handle as N increases, and for polydisperse polymers with a large number of chain lengths an explicit expression can be derived from it only in special cases.[4] Fortunately, as Irvine and Kennedy have shown in their recent paper,[5] there exists a general method of computing phase diagrams for systems with polymers of arbitrary polydispersity. The method involves free energy functions of the Flory–Huggins[6] type

$$\Delta G_{mix}/\mathcal{N}_1 RT = \sum_{i=0}^{N} \phi_i m_i^{-1} \ln \phi_i + \Gamma \tag{2}$$

and exploits the expansion of the appropriate conditions (e.g., eq 1 for the spinodal) in terms of moments of the unnormalized molecular weight distribution, defined as[7]

$$M_k \equiv \sum_{i=1}^{N} \phi_i m_i^k \tag{3}$$

$\mathcal{N}_1$ is the number of lattice "moles" and m_i is the length of the ith chain relative to the size of a solvent molecule (subscript "0"; $m_0 = 1$).

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