Partial Methylation of Poly[thio-1-(*N,N*-dimethylaminomethyl)ethylene] and Conformational Behavior of Resulting Dibasic Polyelectrolytes

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ABSTRACT: The quaternization of some of the side-chain tertiary amine groups of poly[thio-1-(*N,N*-diethyl aminomethyl)ethylene] (P TDAE) was attempted in order to water-solubilize the weak polybases regardless of the pH. CH_3I readily quaternized amino groups but a simultaneous degradation of the polythioether backbone occurred. Methylating conditions were adjusted to limit the decrease in molecular weight. Copolymers having 17, 22, 35, and 48% (Q-P TDAE 17, 22, 35, and 48) of quaternized repeat units were prepared. The addition of HCl to solutions of these compounds (dibasic form) gives rise to: first, an ion-exchange reaction on quaternary ammonium groups: $\text{NR}_4^+ \text{OH}^- \rightleftharpoons \text{NR}_4^+ \text{Cl}^-$, and second, a protonation reaction of tertiary amine groups. Only the latter increases the charge density of the polymer chains. The resulting changes in pH and viscosity are discussed. Surprisingly, for Q-P TDAE 17 and 22, a high buffering region similar to that found for precipitating P TDAE, was observed on potentiometric titration curves in the zone corresponding to the protonation of tertiary amine groups. Further, viscometric titration curves exhibited a linear variation of the reduced viscosity in the same zone. Neither of these features appeared for Q-P TDAE 35 and 48, or in 80:20 (v/v) methanol–water mixture, whatever the degree of quaternization. A polysoap-like to extended coil conformational transition with an all-or-nothing cooperative mechanism is proposed to account of particularities in the physicochemical behavior of Q-P TDAE 17 and 22.

KEY WORDS Polyamines / Quaternization / Partially Quaternized Poly(tertiary amine)s / Dibasic Polyelectrolytes / Conformational Transition / Cooperativity / Buffering Effect /

As a part of our research on the effect of chemical reactions on chiroptical properties of optically active polymers other than biopolymers,¹ we have been interested, in the past years, in the study of poly[thio-1-(*N*- R_1 ,*N*- R_2 -aminomethyl)ethylene]s (I), a new series of ionizable polymers composed of a polythioether backbone and of tertiary amine side-chains^{2–3}:

The goal of this study is to correlate changes in potentiometric, viscometric, and chiroptical properties with the protonation of amino sites by acids in

aqueous medium. However, investigations are limited by the precipitation of polymer chains which occur early when deprotonating nitrogen atoms of the water-soluble polyhydrochloride form by the addition of an alkaline reagent.⁴

The high buffering region observed in potentiometric titration curves during the precipitation has been assigned to the phase separation of almost completely deprotonated macromolecules at equilibrium with highly protonated ones which remain in solution,⁴ as already suggested in the case of poly(*N,N*-diethylaminoethylmethacrylate).⁵ For the latter compound,⁶ as with poly(vinylpyridine)⁷ and many other water-insoluble polytertiary amines,⁸ it has been shown that the presence of quaternary ammonium groups even in a relatively low proportion, results in the water-solubilization of these macromolecules. Basically, the solubilizing effect of a

few permanently ionized groups could provide us with the possibility of studying the acid-base behavior of the remaining tertiary amine residues of partially quaternized poly[thio-1-(N - R_1 , N - R_2 -aminomethyl)ethylene]s throughout the whole range of the degree of protonation β .

As an exploratory step, the case of racemic poly[thio-1-(N , N -diethylaminomethyl)ethylene], the simplest member of the series of poly[thio-1-(N - R_1 , N - R_2 -aminomethyl)ethylene] polybases, has been considered.

In this paper, we wish to report the synthesis of partially quaternized poly[thio-1-(N , N -diethylamino methyl)ethylene] and the investigation by potentiometry and viscometry of acid-base properties of these particular polyelectrolytes whose macromolecules bear strong and weak basic groups randomly distributed.

EXPERIMENTAL

Materials

Poly[thio-1-(N , N -diethylaminomethyl)ethylene] (PTDAE). Samples of high-molecular-weights PTDAE were prepared by ring opening polymerization of N , N -diethyl- N -(thiirane-2-ylmethyl) amine (TDAE) either in bulk (anionically initiated on a Na film⁹) or in toluene (initiated by the 1:1.92 ZnEt₂-MeOH system²). The purification of the polymers was conducted as already reported.² Resulting polymers in the deprotonated form being not stable for a long time at room temperature, samples were turned to the hydrochloride form by blowing dried HCl into a 40:60 (v/v) benzene-ether solution. After filtration, precipitated polyhydrochloride samples were kept in a dessicator at room temperature.

Partially Quaternized Copolymers (Q-PTDAE). Methylation was carried out at room temperature on the deprotonated form of PTDAE in benzene and on the partially protonated forms in benzene-methanol mixtures. The polyhydrochloride form in water resumed the polyamine form on adding 1 M NaOH with further purification of the precipitated polybase through a benzene-methanol solvent-non solvent system. Samples of partially protonated polyamines were directly obtained by adding the convenient amount of sodium methoxide to solutions of the protonated polyamine in methanol with further addition of benzene to obtain a

40:60 (v/v) methanol-benzene mixture. The alkylating reagent was then added, and the mixtures were stirred for the definite reaction time. After acidification by HCl, the different mixtures were dialyzed against methanol through a semipermeable cellulose membrane. The solvent of the dialyzed solutions was evaporated with further vacuum drying to yield completely protonated copolymers in a white-powdered form.

The deprotonation of tertiary amine groups and the $\text{Cl}^- \rightleftharpoons \text{OH}^-$ ion-exchange on quaternary ammonium groups were carried out by percolating concentrated aqueous solutions of the different protonated copolymers through an anion-exchange column filled up with a BIO-RAD-AG 1 $\times$ 4 100—200 mesh resin (OH^- form). Collected basic solutions were titrated and then diluted to convenient concentrations.

MEASUREMENTS

Titration and Determination of the Degree of Quaternization

Basic percolated solutions ($T_N \cong 1.5 \times 10^{-2} N$) were titrated under N_2 atmosphere with a 1 M HCl solution by using a pH M-52 Radiometer pH-meter fitted with a combined glass electrode standardized at pH=4.005 (5×10^{-2} M potassium biphthalate buffer) and at pH=9.196 (5×10^{-2} borax solution). Titration curves exhibited two drops in potential. The first one, observed at a volume V_1 of titrating reagent, corresponded to the neutralization of quaternary ammonium hydroxide groups. The second drop, observed at V_2 , corresponded to the neutralization of all the basic groups (ammonium hydroxide + tertiary amine). The degree of quaternization τ was then given by $\tau = V_1/V_2$.

Viscosity

The reduced viscosity of Q-PTDAE's solutions was measured at 25°C in a viscomatic FICA automatic viscometer. Measurements at various values of the degree of neutralization were performed by adding 1 M HCl to diluted solutions of polymers. The effect of dilution by the titrating reagent was corrected proportionally.

RESULTS AND DISCUSSION

Partial Quaternization of PTDAE

The partial quaternization of PTDAE was first

attempted by using methyl iodide known as an efficient methylating reagent.¹⁰ Different experimental conditions (reaction time, and $[\text{ICH}_3]/[\text{N}-(\text{C}_2\text{H}_5)_2]$ ratios) were considered in order to vary the proportion of quaternized repeating units. Results of these preliminary experiments are given in Table I (runs 1–4).

After the conversion of ammonium groups to their hydroxylated form by percolating aqueous solutions through an anion-exchange column (OH^- form), the degree of quaternization τ of the different compounds was determined by potentiometric titration of strong and weak basic groups.

The insolubility of copolymers in ordinary organic solvents whatever the ionic state, dictated the measurement of viscosity in water. In that solvent, most of the copolymers in the protonated form behaved as polyelectrolytes as shown in Figure 1. However the specific viscosity of the different copolymers for a given concentration obviously decreased with increasing τ although the charge density was the same. Further, no polyelectrolytical effect was ob-

served for compounds with high τ values. These trends were supposed to result from a degradation reaction affecting the polythioether backbone simultaneously to the *N*-methylation reaction. This assumption is supported by the fact that polymer chains formed during the course of cationic polymerization of thiiranes by triethyloxonium tetrafluoroborate (a known alkylating reagent¹¹) are further degraded because of an intramolecular nucleophilic attack on sulfonium sites.^{12–13} It is likely that ICH_3 , which alkylated amino sites of PTDAE, was capable of alkylating sulfide sites as well, thus providing the required conditions for a cationic degradation of polythioether chains. The attack of the backbone of PTDAE's was indirectly confirmed by the behavior of a sample of high-molecular-weight poly(propylene sulfide) in the presence of ICH_3

in benzene. Indeed, the viscosity of the solution, initially $\eta_{sp}/c = 0.8$ (for $c = 1\%$), fell down to 0.4 after 48 h.

In attempting to reduce the effect of the degradation reaction with regard to the expected quaternization of amino groups, different factors were modified:

- (i) the solvent (benzene + acetonitrile) for the amine form, (benzene + methanol) for the hydrochloride form;
- (ii) the alkylating reagent (ICH_3 , BrCH_3 , $\text{SO}_4(\text{CH}_3)_2$);
- (iii) the molecular weight of the starting poly(tertiary amine) and its degree of protonation.

On the basis of the reduced viscosity of fully protonated copolymers ($c = 1\%$), it was concluded that:

- (i) dimethyl sulfate is less degrading than methyl iodide and methyl bromide;
- (ii) the presence of a small amount of a polar solvent enhanced the efficiency of alkylating reagent. No *N*-methylation was detected when tertiary amino groups were fully protonated.

So far, we have not succeeded in our attempt to prevent the degradation reaction. Anyway, different partially quaternized copolymers of sufficient molecular weights to permit meaningful physicochemical investigations were prepared as follows. The meth-

Figure 1. Effect of methylation by methyl iodide on the reduced viscosity of PTDAE's in water (protonated form): $\circ$ —, PTDAE; $\blacktriangledown$ —, Q-PTDAE 11; $\triangle$ —, Q-P TDAE 15; $\square$ —, Q-PTDAE 41; $\bullet$ —, Q-PTDAE 75.

Table 1. Partial methylation of poly[thio-1-(*N,N*-diethyl aminomethyl)ethylene] (PTDAE)

Run no.	$\frac{\eta_{sp}}{c^a}$ 100 cm ³ g ⁻¹ (Starting polymer)	Solvent	Repeating units, Concentration $\times 10^{-3}$ M l ⁻¹	Methylating reagent, CH ₃ X	$\frac{[CH_3X]}{[units]}$	Reaction time h	$\frac{\eta_{sp}}{c^a}$ 100 cm ³ g ⁻¹ (Resulting copolymer)	Degree ^b of quaternization
1	1.30	Benzene	0.6	CH ₃ I	0.11	48	1.10	0.10
2	"	"	"	"	0.19	48	0.58	0.15
3	"	"	"	"	0.55	48	0.35	0.41
4	"	"	"	"	1.10	72	0.20	0.75
5	20 ^{c,f,h}	Benzene–methanol 60/40 (v/v)	1.6	(CH ₃) ₂ SO ₄	1	24	4.10 ^h	0.17
6	20 ^{c,f,h}	"	"	"	1	48	2.00 ^h	0.22
7	80 ^{d,g,h}	"	"	"	1	24	0.95 ^h	0.35
8	80 ^{e,g,h}	"	"	"	1	24	0.60 ^h	0.48
9	80 ^{e,g,h}	"	"	"	1.3	24	0.58 ^h	0.52

^a Reduced viscosity of the protonated form in water ($c = 1 \text{ g} \cdot 100 \text{ cm}^{-3}$) at 25°C.^b Deduced from potentiometric titration curves by 1 M HCl of copolymers percolated through an anion-exchange column (form OH⁻).^c Polyhydrochloride form 50% deprotonated by sodium methoxide.^d Polyhydrochloride form 60% deprotonated by sodium methoxide.^e Polyhydrochloride form 70% deprotonated by sodium methoxide.^f $M_n \cong 2.2 \times 10^5$ daltons as determined by osmometry of PTDAE in toluene.^g $M_n \cong 4.4 \times 10^5$ daltons as determined by osmometry of PTDAE in toluene.^h Reduced viscosity for the protonated form in water ($c = 0.5 \text{ g} \cdot 100 \text{ cm}^{-3}$).

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ylation reaction was carried out on partially protonated PTDAE of initial high molecular weights by using dimethylsulfate in a benzene-methanol solvent mixture (Table I, runs 5–9). After conversion to their fully protonated forms, the resulting copolymers were dialyzed against methanol in order to eliminate the smallest fragment of degraded macromolecules. Copolymers Q-PTDAE with 17, 22, 35, 48, and 52% of quaternized repeating units were obtained by this method. Although their molecular weights were not determined, all of them can be considered as polymers because they exhibited a polyelectrolytical effect when fully protonated. Compounds with 17, 22, 35, and 48% of quaternized units (Q-PTDAE 17, 22, 35, and 48) were selected for

the rest of the work.

Acid-Base Properties

Free tertiary amine groups and positively charged groups are present in Q-PTDAE's. The behavior of positively charged groups depends on counterions. When neutralized by anions derived from strong acids like HCl, HBr, etc., quaternary ammonium groups behave as neutral salts, though they are strongly basic, when counterions are OH^- ions. In the latter case, which is obtained by percolating protonated copolymer solutions through an anion-exchange column (OH^- form), the neutralization by strong acids (HX) can be represented in two steps as follows.

Step 1: Ion-exchange on quaternary ammonium groups

Step 2: Protonation of tertiary amine groups

where K_a is the dissociation constant of protonated amino-groups and K_b is the protonation constant of the tertiary amine ones.

During step 1 (ion-exchange), the number of ionized repeating units defined by the degree of quaternization τ , remained constant. In contrast, the protonation of tertiary amine groups (step 2) increased the charge density of macromolecules. Given the presence of two types of basic units, the following parameters were considered to describe the action of HX on the polybasic form of partially quaternized PTDAE.

(i) ε is the degree of neutralization of the hydroxylated quaternary ammonium groups;

(ii) β is the degree of protonation of tertiary amine groups. These basic groups being of medium

strength, β was considered as equal to the normality of the strong acid added beyond the neutralization of strong basic groups divided by the normality of tertiary amine repeating units;

(iii) δ is the degree of neutralization of all the basic repeating units in the dibasic form of Q-PTDAE's, $\delta = [\text{HCl}]/T_N$;

(iv) γ is the molar fraction of the ionized monomeric units $\gamma = \tau + \beta(1 - \tau)$ which can be assimilated to a degree of ionization if all the positive charges are assumed equivalent.

Potentiometry in Salt-Free Water Solution. The neutralization of the various copolymers (dibasic form) by HCl was first monitored by pH-metry. The potentiometric curves are shown in Figure 2 for $0 < \delta < 1$.

Figure 2. Potentiometric titration curves of dibasic Q-PTDAE 17 (∇); 22 ($\blacktriangle$); 35 ($\circ$) and 48 ($\bullet$) ($T_N = 1.5 \times 10^{-2}$ N) and of PTDAE [$\blacksquare$, $T_N = 2 \times 10^{-2}$ N, in water (titrating reagent, 1 M HCl)].

For comparison purposes, the potentiometric curve of the non-quaternized polyamine is also included. That curve exemplifies the high buffering region previously assigned to a phase separation of completely deprotonated macromolecules.⁴ For partially quaternized polyamines, the potentiometric curves showed two potential drops corresponding to the successive neutralization of the strong and weak basic groups already discussed. The protonation of the tertiary amine groups is included between these two drops. For Q-PTDAE 35 and 48, no plateau was observed. However, curves corresponding to Q-PTDAE 17 and 22 present a plateau similar to that observed for the non-quaternized polyamine, though of a shorter length. The presence of this plateau is surprising because the medium is apparently homogeneous, the optical density never exceeded 0.05 at 400 nm.

A theoretical analysis of the behavior of polyelectrolytes leads to the general potentiometric equation for polymer bases:

$$\text{pH} = \text{p}K'_0 - \log \frac{\beta}{1-\beta} - \frac{0.434}{kT} \times \frac{\delta G_e}{\delta \xi} \quad (1)$$

where $\text{p}K'_0$ is the dissociation constant of the cationic acid conjugate to the single basic group of the polymer, β is the degree of protonation of the polybase and ξ is the number of positive ionized groups carried by each polyelectrolyte molecule.¹⁴

Equation 1 is equivalent to eq 2

$$\text{pH} = \text{p}K_{\text{aapp}} - \log \frac{\beta}{1-\beta} \quad (2)$$

where $\text{p}K_{\text{aapp}}$ is the apparent dissociation constant of the cationic acid conjugate to the single basic group for a given β value.

Similarly, the reaction of protonation of single basic groups of the polybase in water can be characterized by the apparent protonation constant $\text{p}K_{\text{bapp}}$ according to eq 3

$$\text{p}K_{\text{bapp}} = 14 - \text{p}K_{\text{aapp}} \quad (3)$$

In the following, potentiometric data have been expressed in terms of $\text{p}K_{\text{bapp}}$ which allows direct comparison of the polyelectrolytical behavior of polybases and of polyacids.

For partially quaternized polytertiary amines, permanent electric charges due to quaternary ammonium groups contribute to the electric potential of the polyion and thus, they perturb the ionization behavior of the weak basic tertiary amine groups. To take into account the presence of these permanent charges in Q-PTDAE's, variations of $\text{p}K_{\text{bapp}}$ of tertiary amine groups have been represented against γ , assuming that methylated and protonated monomeric units are equivalent from the viewpoint of electrostatic effects.

Plots of $\text{p}K_{\text{bapp}}$ vs. γ as deduced from titration curves of Q-PTDAE 17, 22, 35, and 48 shown in Figure 2 and from eq 2 and 3 are represented in Figure 3.

$\text{p}K_{\text{bapp}}$ of Q-PTDAE 17, 22, and 35 first decreased as γ increased. The trend was reversed for $\gamma > 0.8$. In contrast, $\text{p}K_{\text{bapp}}$ of Q-PTDAE 48 increased over the whole range of the neutralization of tertiary amine groups as usual for conventional polyelectrolytes.¹⁵ It is worth to note that for high γ values ($\gamma > 0.8$) the four curves joined together, i.e., the four polybases which are electrostatically very similar behaved almost identically.

Figure 3. Variations of pK_{bapp} vs. γ of dibasic Q-PTDAE 17 (∇); 22 ($\blacktriangle$); 35 ($\circ$) and 48 ($\bullet$); ($T_N = 1.5 \times 10^{-2}$ N, in water (titrating reagent, 1 M HCl).

Potentiometry in Salt-Containing Water Solution. Titration curves monitored by pH-metry were obtained for various values of the ionic strength. Plots of pK_{bapp} against γ for the different Q-PTDAE's and at various KCl concentrations are represented in Figure 4. The presence of salt strengthened the basicity of tertiary amine groups, as it is usually observed for weak polyelectrolytes. Further Q-PTDAE 17 and 22 were salted out at $C_{KCl} > 0.3$ and 1×10^{-1} M respectively, while compounds with $\tau = 35$ and 48% did not precipitate in the range of concentrations considered.

For moderately hydrophobic polyacids which show compactly coiled conformations at low values of the degree of ionization α , the presence of salt strengthens the acidity and it flattens the $pK_{aapp} = f(\alpha)$ curves as compared to a salt-free system. Further, there is an increase in the degree of ionization α_m corresponding to the end of the compact coil-to-extended coil transition. These features have been interpreted as the evidence for a stabilization of compact conformation because of a salt effect on repulsive electrostatic charges.¹⁶

As shown in Figure 4 similar trends were observed

Figure 4. Influence of ionic strength on the potentiometric titration curves of dibasic Q-PTDAE 17 (∇); 22 ($\blacktriangle$); 35 ($\circ$) and 48 ($\bullet$); $T_N = 0.5 \times 10^{-2}$ N, in water (titrating reagent, 1 M HCl); [$C_{KCl} = 0$ (—); $C_{KCl} = 0.5 \times 10^{-2}$ M l^{-1} (---); $C_{KCl} = 3 \times 10^{-2}$ M l^{-1} (- · -); $C_{KCl} = 10^{-1}$ M l^{-1} (— —); $C_{KCl} = 3 \times 10^{-1}$ M l^{-1} (·····)].

for Q-PTDAE 17, 22 and 35 if one assumed that the points where $\delta pK_{bapp}/\delta\gamma \approx 0$ have the same meaning as α_m . In $pK_{bapp} = f(\gamma)$ curves corresponding to Q-PTDAE 48, the effect was emphasized since the slope which was positive for low ionic strength values, became negative for $C_{KCl} = 3 \times 10^{-1}$ M. Actually, this discussion is meaningless for Q-PTDAE 17 and 22 because the system cannot be considered as homogeneous in a wide range of γ values as it is shown by the following.

Viscometry. Reduced viscosity was measured under conditions similar to those selected for potentiometric investigations. Variations of η_{sp}/c of Q-PTDAE's during the neutralization of strongly and weakly basic groups are represented in Figure 5. The results were plotted against ϵ and β so as to emphasize the drastic effect of the ionization of tertiary amine groups. The effect of the polymer

concentration and that of the ionic strength on the reduced viscosity of low τ Q-PTDAE's is exemplified in the case of Q-PTDAE 22.

Neutralization of Strongly Basic Groups

For the hydroxylated form of compounds 17, 22, and 35, the reduced viscosity was very low (<0.2 $100\text{ cm}^3\text{ g}^{-1}$) and independent of the degree of quaternization. Further, the values of η_{sp}/c for these three compounds were significantly lower than that of Q-PTDAE 48 although the latter certainly had much lower molecular weight, because of the degradation reaction as mentioned above. These features support the compactly coiled form for Q-PTDAE 17, 22, and 35. As ϵ increased from 0 to 1, OH^- ions were replaced by Cl^- ions, and the number of ionized groups did not change. Macromolecules remained compactly coiled as indicated by the low values of the reduced viscosity.

Neutralization of Weakly Basic Tertiary Amine Groups

As soon as tertiary amine groups ionized as a result of adding the HCl solution, the reduced viscosity of Q-PTDAE 17 and 22 sharply increased with β . It is noteworthy that η_{sp}/c varied linearly in the range of β , which corresponds to the plateau in the potentiometric titration curves (Figure 2). For Q-PTDAE 35 and 48 whose potentiometric titration curves showed no plateau, the change in η_{sp}/c as a function of β was not linear. Curves resembled those corresponding to conventional polyelectrolytes.¹⁷ For Q-PTDAE 48, the change in η_{sp}/c with β was relatively small. This trend is certainly due to the fact that macromolecules were already extended because of the large proportion of permanently charged units ($\cong 50\%$).

It is worth to note that neither the polymer concentration nor the salt concentration affected the reduced viscosity of Q-PTDAE 22 in the range where ammonium hydroxide groups were neutralized. In contrast, drastic effects of both factors were found in the zone where tertiary amine groups were protonated (Figure 5).

Among the results of potentiometric and viscometric investigations of acid-base properties of the four partially quaternized polytertiary amines reported herein, there were several that had to be considered as unusual with regard to the behavior of conventional polyelectrolytes:

Figure 5. Viscometric titration curves of dibasic Q-PTDAE 17 (∇); 22 ($\blacktriangle$); 35 ($\circ$) and 48 ($\bullet$) in water (titrating reagent, 1 M HCl).

$$\text{Q-P TDAE 22} \left\{ \begin{array}{l} T_N = 1.5 \times 10^{-2} \text{ N}, C_{\text{KCl}} = 0 \text{ (—)} \\ T_N = 0.5 \times 10^{-2} \text{ N}, C_{\text{KCl}} = 0 \text{ (- · -)} \\ T_N = 0.5 \times 10^{-2} \text{ N}, \\ \quad C_{\text{KCl}} = 0.5 \times 10^{-2} \text{ M l}^{-1} \text{ (----)} \\ T_N = 0.5 \times 10^{-2} \text{ N}, \\ \quad C_{\text{KCl}} = 1 \times 10^{-2} \text{ M l}^{-1} \text{ (- · · -)} \\ T_N = 0.5 \times 10^{-2} \text{ N}, \\ \quad C_{\text{KCl}} = 3 \times 10^{-2} \text{ M l}^{-1} \text{ (·····)} \end{array} \right.$$

1) the very low value of η_{sp}/c for deprotonated Q-PTDAE 17, 22, and 35;

2) the absence of the effect of the ionic strength on η_{sp}/c in the range of the $\text{OH}^- \rightarrow \text{Cl}^-$ ion-exchange reaction;

3) the presence of a high buffering region on the potentiometric titration curves of Q-PTDAE 17 and 22 in the zone of the protonation reaction though no precipitated phase was detected.

4) the linear variation of η_{sp}/c with β on the viscometric titration curves in the zone corresponding to the plateau of pH in potentiometric ones.

However, the most striking feature is the difference between the methylation and the protonation of nitrogen groups in terms of capacity for acting as water-solubilizing PTDAE chains. While β values as

high as 0.9 were needed to completely solubilize non-quaternized PTDAE in water,⁴ a few percent of methyl ammonium groups was apparently sufficient to bring about the same effect.

To account for the low value of η_{sp}/c for Q-PTDAE 17, 22 and 35 for $\beta=0$, it is suggested that macromolecules take on a globular polysoap-like compact conformation stabilized by permanent positive charges ($\geq N^+-CH_3$) which locate at the surface (microemulsion). Comparing Figures 2 and 5, the high buffering region observed on the potentiometric titration curves and the linear variation of η_{sp}/c with β on the viscometric curves distinguished Q-PTDAE 17 and 22 from the compound with repeating units methylated 35%.

For water-insoluble non-quaternized poly(*N,N*-diethylaminoethyl methacrylate),⁵ and PTDAE,⁴ the high buffering region observed on the potentiometric titration curves has been assigned to the precipitation of the almost totally deprotonated macromolecules at equilibrium with the soluble ones whose actual degree of protonation β^* depended on the polymer concentration in the solution phase. For poly(*N,N*-diethylaminoethyl methacrylate),⁵ it has been shown that the following equation

$$pH - pH_{(pp \text{ pt})} = 1/\langle P \rangle \int_{c_{m(pp \text{ pt})}}^{c_m} 1/\beta^* (d \log c_m) \quad (4)$$

(where $\langle P \rangle$, β^* , and c_m are respectively the average degree of polymerization, the degree of protonation, and the monomolar concentration of macromolecules located in the solution phase) holds if the chemical potential of the precipitate remains independent of the pH, and activity coefficients of all the species of the polyelectrolyte in solution remain practically constant.¹⁸

Similarly, to account for the presence of the

plateau on the potentiometric titration curves of soluble Q-PTDAE 17 and 22, it is assumed that, in the corresponding range of β values, the macromolecules are actually distributed in a two-phase system, *i.e.*, solvated and highly protonated Q-P TDAE macromolecules at equilibrium with deprotonated macromolecules located in a separated but not macroscopically precipitated phase. Since the existence of polysoap-like globules is supported by viscometric measurements at $\beta=0$, it is believed that the inner part of these globules in which deprotonated segments of tertiary amine repeating units stick together, constitutes the required water-free separated phase with a fixed chemical potential.¹⁹

This system is thus similar to that given by water-insoluble polytertiary amines, but without macroscopic precipitation. The adding of H^+ or OH^- to that system changes the distribution of macromolecules between the two phases according to scheme I.

This particular kind of behavior results from the lability of $N \rightarrow H$ bonds as compared to the covalent N^+-CH_3 bonds. Indeed, the lability of $N \rightarrow H$ bonds allows the migration of protons, and thus that of corresponding electric charges from one tertiary amine residues to the other. Therefore, hydrophobic interactions between deprotonated tertiary amine residues (for extended macromolecules) or electrostatic repulsive forces between protonated residues (for globules) can act cooperatively to strip soluble macromolecules of protons or to free tertiary amine residues hidden within globules. This process, which is similar to cooperative conformational transitions of biopolymers,²⁰ involves solvation, protonation, and hydrophobic interactions phenomena. However, no structural order is expected for the globular form, the configurational stereoregularity of parent PTDAE macromolecules being low as already shown.²¹

Scheme I. Schematic representation of macromolecules in the water-free globular conformation and of those in the highly protonated extended state at equilibrium in the two-phase system.

For polytertiary amines, it has been shown that β^* is almost constant in a wide range of values corresponding to the average degree of protonation in the two-phase system.⁴⁻⁵ It is likely that a similar trend exists for Q-PTDAE 17 and 22. In that zone, macromolecules in the solution phase are in well defined chemical and conformational states. Therefore, the system behaves through an all-or-nothing mechanism. Such a mechanism accounts for the linear variation of the reduced viscosity with β which can be considered as consisting additively of the value for the two limiting structures (*e.g.*, for the globular and the extended state).²⁰

Comparing data for Q-PTDAE 17 and 22, it is obvious that the higher the τ value, the smaller the length of the plateau of pH, *i.e.*, the smaller the zone of the two-phase system.

For Q-PTDAE 35, a compact conformation still existed for $\beta=0$, but the higher density of randomly distributed $\geq N-R_4^+$ quaternary ammonium units prevented the total expulsion of water from the inner part of the globules. When the titrating reagent was added, the system changed through the usual progressive process reported for hydrophobic polyacids²² where the chemical potential of the globular phase cannot be considered as independent of the H^+ activity.

For Q-PTDAE 48, macromolecules were in a rather extended state, even for $\beta=0$, because of the high content in fixed ammonium groups. This compound behaved as a conventional polyelectrolyte in so far as the weakly basic groups were concerned.

Scheme II summarizes the qualitative interpretation given above on the acid-base properties of Q-PTDAE's for various values of τ and γ as deduced from the plateau observed on the potentiometric curves (Figure 2). In that scheme, γ_1 and γ_2 which correspond to the γ values at the extremities of the plateau have been considered as the boundaries of the two-phase domain *i.e.*, values at which all the macromolecules are in the globular state and in the extended state, respectively. From the variation of γ_1 and γ_2 with τ in Scheme II, it is deduced that the two-phase zone vanishes at $\tau \approx 0.33$. The fact that γ_1 is higher than τ is probably due to a few tertiary amine groups localized at the surface of globules which can protonate without destabilizing the compact structure. Accordingly, the scheme can be decomposed into four domains whose limits are still vague. Domains 1 and 2 correspond to the water-free and

Scheme II. Polyelectrolytical behavior of Q-PTDAE's, with regard to the degree of quaternization and to the molar fraction of charged units in macromolecules, as defined from γ_1 and γ_2 deduced from extremities of the plateau of pH observed in potentiometric titration curves.

① domain of water-free globular conformation
 ② domain of water-containing globular conformation
 ③ domain of the two-phase system
 ④ domain of conventional polyelectrolytical behavior
 (Experimental data: $\square$, PTDAE; ∇ , Q-PTDAE 17; $\blacktriangle$, Q-PTDAE 22; $\circ$, Q-PTDAE 35; $\bullet$, Q-PTDAE 48; $\diamond$, γ_1 ; $\blacklozenge$, γ_2)

solvated compactly coiled conformations, respectively. The two-phase zone constitutes domain 3, while in domain 4, charged macromolecules behave as conventional polyelectrolytes.

It is worth pointing out that for γ values higher than γ_2 , the soluble partially protonated macromolecules must behave identically, regardless of the degree of quaternization τ . This is the case as shown by $pK_{bapp} = f(\gamma)$ curves plotted in Figure 3, in which the curves meet at high γ values. These curves and thus pK_{bapp} values, are obviously meaningless in the zone of γ values corresponding to the plateau of pH *i.e.*, in the two-phase system. For Q-PTDAE 35, the system behaved normally and the curve $pK_{bapp} = f(\gamma)$ was significant. However, it could not be used to characterize the compact coil-to-extended coil conformational transition as in the case of polyacids,²³ the extrapolation to pK_0 being not reasonably possible.

So far, the particular behavior of Q-PTDAE's with a low content of quaternary ammonium groups, based on a comparison with water-insoluble polytertiary amines, is supported by potentiometric and viscometric measurements mostly carried out in

Figure 6. Potentiometric titration curves of dibasic Q-PTDAE 17 (∇); 22 ($\blacktriangle$); 35 ($\circ$) and 48 ($\bullet$); $T_N = 1 \times 10^{-2}$ N; in 40:60 (v/v) methanol-water (—) and in 80:20 (v/v) methanol-water (---) mixtures (titrating reagent, 1 M HCl).

salt-free water, *i.e.*, under conditions where eq 4 is ruled out since the activity coefficients of the different species in solution can not be considered as constant. Further, macromolecules being certainly polydisperse in molecular weight and in chemical composition, the phenomena reported herein are obviously average. In order to qualitatively support the proposed interpretation, the acid-base behavior of Q-PTDAE's was studied in the presence of methanol, a solvent known to destabilize compactly coiled structures due to hydrophobic interactions.²²

Figure 6 represents potentiometric titration curves of Q-PTDAE 17, 22, 35 and 48 in 40:60 (v/v) methanol-water and 80:20 (v/v) methanol-water mixtures. While a plateau was still observed for Q-PTDAE 17 and 22 in the former solvent system, no plateau was evidenced in the latter system and the curves resembled those of Q-PTDAE 35 and 48. Further, Figure 7 represents viscometric titration curves of Q-PTDAE 22 in water, 40:60 (v/v)

Figure 7. Viscometric titration curves of Q-PTDAE 22 ($T_N = 1 \times 10^{-2}$ N): in water ($\blacktriangle$); in 40:60 (v/v) methanol-water ($\cdots\blacktriangle\cdots$) and in 80:20 methanol-water ($\cdots\blacktriangle\cdots$) media (titrating reagent, 1 M HCl).

methanol-water and 80:20 (v/v) methanol-water media. For a given γ value in the protonation region, values of the viscosity were lower in the presence of 40% methanol than in pure water because of the decrease in the dielectric constant of the medium which reduces the net-charge of macromolecules. In the 80:20 (v/v) methanol-water system, the reduced viscosity at $\gamma = 0.22$ ($\beta = 0$) was much higher than in water, thus showing that macromolecules were in a solvated randomly coiled state, and not in a compactly coiled state. Further, the variation of η_{sp}/c with γ (or β) was not linear and resembled that expected for a conventional polyelectrolyte.

CONCLUSIONS

As expected, the partial quaternization of PTDAE water-solubilized deprotonated polytertiary amine segments. However, the study of acid-base properties of Q-PTDAE's in their dibasic form, and especially the effect of protonation of weakly basic tertiary amine groups gave evidence of compounds having the peculiarity of a low content of per-

manently charged repeating units. The two-phase system is proposed to account for potentiometric and viscometric data and resembles cooperative conformational transitions of proteins with an all-or-nothing type of mechanism. This sort of mechanism points to a very high degree of cooperativity between neighboring tertiary amine repeating units in the protonation-deprotonation equilibrium. Finally, it is the lability of $N \rightarrow H^+$ bonds that explains the difference in the capacity of protonated and methylated ammonium groups to function as water-solubilizing of polytertiary amine chains.

Much more work is needed to characterize the two-phase system. Whether the globular structures are composed by one or several macromolecules is still unknown. The determination of the size and of the net-charge of the globules might allow one to answer to this question. On the other hand, it would be particularly interesting to consider the case of optically active Q-PTDAE with a high degree of configurational regularity to see whether entropic effects can be observed, depending on the stereoregularity, as in the case of globular proteins.

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