

Acid-Base and Chiroptical Properties of Partially Quaternized Optically Active Poly[thio-1-(*N*-(*S*)-*s*-butyl-*N*- methylaminomethyl)ethylene]

Jovanka HUGUET, Didier VALLIN, and Michel VERT

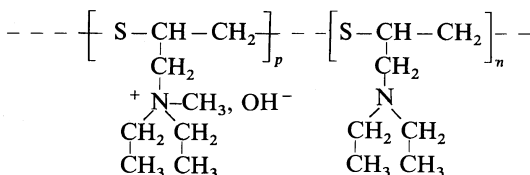
*Laboratoire de Chimie Macromoléculaire, ERA CNRS n°471,
Faculté des Sciences et des Techniques, Université de Haute-Normandie,
76130 Mont-Saint-Aignan, France.*

(Received May 26, 1981)

ABSTRACT: Investigation was made of the effects of counterion exchange at quaternary ammonium sites and of protonation of residual tertiary amine groups on ORD and CD of partially quaternized poly[thio-1-(*N*-(*S*)-*s*-butyl-*N*-methylaminomethyl)ethylene]s in water and in 80:20 v/v methanol-water mixture. Each repeating unit of this type of optically active copolymers bears two chiral centers, one in the main chain and one in the side-chain. The present study is limited to copolymers rendered optically active through side-chain chirality, the main-chain chiral centers being *racemic*. Compounds with 4 and 7% methylated tertiary amine groups (Q-P(TBMAE)_R^{S*} 4 and 7 respectively)[†] are considered. It is shown that deprotonated Q-P(TBMAE)_R^{S*} 7 is slightly aggregated in water. The protonation of tertiary amine residues destabilizes the aggregates and then proceeds non-conventionally through a two-phase mechanism similar to a cooperative conformational transition. ORD and CD do not reflect the particular conformational behavior of Q-P(TBMAE)*. The acid-induced chiroptical property changes depend on the content of charged repeating units only. Comparison is made with Q-P(TDAE)* 17, an *N,N*-diethyl homologue of Q-P(TBMAE)*s, whose optical activity is caused by main chain chiral centers only.

KEY WORDS Synthetic Polyamines / Partially Quaternized Poly(tertiary amines) / Dibasic Polyelectrolytes / Cooperative Conformational Transition / Cooperativity / Buffering Effect / ORD/ CD / Optically Active Polymer / Polybases /

The acid-base properties of optically inactive, partially quaternized poly[thio-1-(*N,N*-diethylaminomethyl)ethylene], (Q-P(TDAE)_X, with *X* = the percentage of quaternized tertiary amine repeating units), have been investigated recently.¹



Q-P(TDAE)_X

We have shown, for the first time, the presence of a plateau similar to that usually observed for precipitating weak polybases² in potentiometric titra-

tion curves of slightly quaternized water-soluble compounds with *X* < 25. In order to account for the presence of a high buffering region in spite of the apparent water-solubility, we suggest that the protonation-deprotonation reaction of the weakly basic groups proceeds through an unusual mechanism based on a microphase separation similar to simultaneous chemical and conformational cooperative transitions of the all-or-none type.¹

Because of the similarity of this mechanism with the denaturation of globular proteins, the question arose as to whether ORD and CD might reflect the particular conformational behavior of slightly quaternized Q-P(TDAE)s. Q-P(TDAE)_R* 17, an optically active *N,N*-diethyl copolymer with predominantly R main chains, (gross optical purity

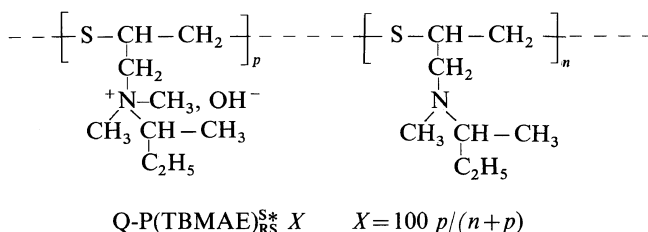
[†] The asterisk indicates that one deals with optically active derivatives.

O.P.=0.27), was synthesized and its chiroptical properties were investigated in regard to the particular acid-base behavior.³ In this case, we have shown that acid-induced ORD and CD changes are directly related to the protonation of tertiary amine groups but do not reflect the ion-exchange at quaternary ammonium sites or the microphase separation in the high buffering region or any order-to-disorder conformational transition in agreement with the low configurational enrichment of the main chains.

The synthesis of Q-P(TDAE)* with high configurational enrichment has not yet been carried out. So, we undertook a study of the effects of

configurational order on acid-base and chiroptical properties in the poly[thio-1-(*N,N*-disubstituted aminomethyl)ethylene] series through homologues of Q-P(TDAE) of the polydiastereoisomeric type, *i.e.* which bear two asymmetric carbon atoms in each repeating unit, one in the main chain and one in the side chain, with the chirality of the latter being under total control.

In this paper, we report our results with partially methylated poly[thio-1-(*N*-(*S*)-*s*-butyl-*N*-methylaminomethyl)ethylene]'s, those members of the series with almost configurationally pure chiral side chains and a racemic main chain (Q-P(TBMAE)_{RS}^{S*}X)^{††}.



The preparation of large amounts of *N*-methylated Q-P(TBMAE)_{RS}^{S*}X with *X* larger than 20 is difficult because of cationic degradation of the polythioether chain during the methylation reaction,¹ and so our present investigation has been limited to compounds with 4 and 7% *N*-methylation, Q-P(TBMAE)_{RS}^{S*} 4 and 7, respectively. Firstly, we studied the acid-base reactions by potentiometry and viscometry. Then, optical activity changes observed during acid-base exchanges were investigated by ORD and CD. The data are discussed in regard to the particular protonation process shown for the first time for Q-P(TDAE)s. In order to comment on structural effects, Q-P(TBMAE)_{RS}^{S*} was compared with Q-P(TDAE)* which has no asymmetric carbon atom in its side chains and different substituents.

EXPERIMENTAL

Materials

Poly[thio-1-(*N*-(*S*)-*s*-butyl-*N*-methylaminomethyl)ethylene], (P(TBMAE)_{RS}^{S*}), was prepared by the polymerization of (*N*-(*S*)-*s*-butyl-*N*-methyl-*N*-

thiirane-2-yl)amine (O.P.=0.94) using the 1:1.9 ZnEt₂/methanol initiator system in a sealed tube at room temperature as already reported.⁴ After purification, the optically active polytertiary amine thus obtained had the following characteristics: [α]_D²⁵ = +26.1 (*c* = 0.73 g dl⁻¹ in benzene) [η] = 0.93 dl g⁻¹ in benzene).

Partially quaternized P(TBMAE)_{RS}^{S*}, (Q-P(TBMAE)_{RS}^{S*}), were prepared by the partial methylation of the sample of P(TBMAE)_{RS}^{S*} using a stoichiometric amount of dimethyl sulfate in a 40:60 *v/v* methanol-benzene mixture at room temperature according to the process used to methylate P(TDAE).¹ Two samples of Q-P(TBMAE)_{RS}^{S*}, with 4 and 7% methylated tertiary amine units, were obtained after 24 and 36 h stirring, respectively. Both samples were conditioned as described in ref 1 for Q-P(TDAE).

Measurements

The potentiometric and viscometric titrations and the determination of the degree of quaternization τ = *n*/(*n* + *p*) were performed as in ref 1.

ORD spectra were recorded with a FICA

^{††} In order to facilitate the understanding of diastereoisomeric species, the predominant configuration of side-chain chiral centers is given as high index while that of main-chain chiral centers is given as low index.

Spectropol I spectropolarimeter thermostated at $25 \pm 0.1^\circ\text{C}$. Data are expressed in terms of mean residue molecular weight, $\text{MRW} = M_1\tau + (1-\tau)M_2$, M_1 and M_2 being molecular weights of *N*-methylated and of non-methylated repeating units respectively. The protonation of tertiary amine groups was not taken into account.

CD spectra were obtained with a JASCO J40B dichrometer at room temperature. Monomolar ellipticity is expressed in terms of MRW.

The determination of M_w was performed with a Chromatix Laser Light Scattering apparatus from data taken at five different concentrations. The values of dn/dc were determined with a Brice-Phoenix differential refractometer.

RESULTS AND DISCUSSION

Because of the presence of both strongly basic (quaternary ammonium) and weakly basic (tertiary amine) repeating units with Q-P(TBMAE) macromolecules, various parameters were introduced, besides X , to define all possible chemical states: ϵ , the degree of neutralization of quaternary ammonium groups referred to as the OH^- form; β , the degree of protonation of tertiary amine groups; $\gamma = X/100 + (1 - X/100)$, the molar fraction of charged repeating units regardless of the particular nature of the unit, and $\delta = \text{added } [\text{H}^+]/\text{normality}$, the total degree of neutralization referred to as the OH^- form.¹ Since the tertiary amine moieties of Q-P(TBMAE)'s are moderately weak basic group types, the approximation $\gamma = \delta$ may be considered correct in the $\delta > \tau$ range. In contrast, $\delta = \epsilon\tau$ and γ remain constant in all $\delta < \tau$ ranges since quaternary ammonium groups are strongly basic.

Acid-Base Properties

Figure 1 shows potentiometric and viscometric titration curves of the Q-P(TBMAE)_{RS}^{S*} 7 (OH^-) form in salt-free water and in salt-free 80:20 v/v methanol-water. In water, a high buffering region corresponding to a linear variation of reduced viscosity was observed as δ increased. In contrast, no buffering effect or linear viscosity variation could be observed in the hydro-organic medium, thus showing that Q-P(TBMAE)_{RS}^{S*} behaves conventionally. These features are similar to those previously found for racemic and optically Q-P(TDAE) 17.^{1,3} However slight differences should

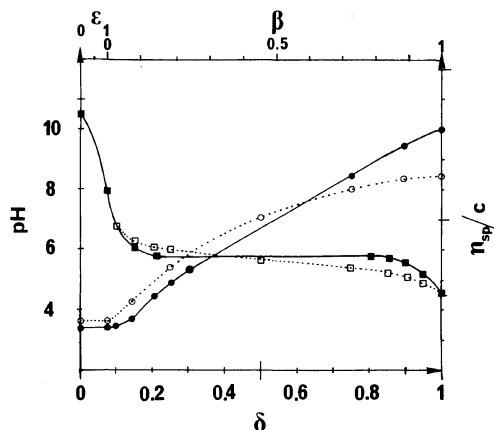


Figure 1. Potentiometric (—■—) and viscometric (—●—) titration curves of Q-P(TBMAE)_{RS}^{S*} 7 in water (—) and in 80:20 v/v methanol-water (---) ($T_N = 1 \times 10^{-2} \text{N}$; titrating reagent 1 M HCl).

be considered. The plateau observed in water for Q-P(TBMAE) 7 and both Q-P(TDAE) 17's begins with the same γ_1 values ($\delta = 0.25$) but ends with different γ_2 values: $\delta \approx 0.75$ for Q-P(TDAE) 17's and $\delta \approx 0.85$ for Q-P(TBMAE)_{RS}^{S*} 7. According to the two-phase model proposed for water-soluble Q-P(TDAE) with low X values ($X < 25$), the higher γ_2 value found for Q-P(TDAE)_{RS}^{S*} 7 reflects a higher stability of the globular organic microphase¹ and thus a higher hydrophobic character.⁵ But, the value of η_{sp}/c for Q-P(TBMAE)_{RS}^{S*} 7 is much higher than that reported for Q-P(TDAE) 17 in the OH^- form while it is lower in the fully protonated form. Also, the bending of the viscometric titration curve of Q-P(TBMAE)_{RS}^{S*} 7 in water in the $0.07 < \delta < 0.25$ range was not observed for Q-P(TDAE) 17's.^{1,3} In order to test whether the particularities of Q-P(TBMAE) are related to differences in structure or to differences in the degree of *N*-methylation, the molecular weight M_w and relative viscosity η_{sp}/c were measured for both the deprotonated and the protonated forms of Q-P(TDAE) 17 and Q-P(TDAE) 7, *i.e.*, for two derivatives of the same type but with different X values. The data are given in Table I.

For Q-P(TDAE) 17, M_w had the same values for both the OH^- and H^+ forms. In this case, the water-free organic microphase, proposed to account for the presence of the high buffering region,¹ is obviously composed of monomolecular globules. In contrast, for Q-P(TDAE) 7, the M_w in the OH^-

Table I. Comparison of molecular weights M_w of Q-P(TDAE) 7 and 17 as determined by laser light scattering

	Q-P(TDAE) 7 ^a		Q-P(TDAE)* 17 ^b	
	OH ⁻ form ^c	H ⁺ form ^d	OH ⁻ form ^c	H ⁺ form ^d
$\frac{\eta_{sp}/c}{\text{dl g}^{-1}}$	0.26 ^e	3.1 ^e	0.03 ^f	5.3 ^f
M_w	450,000	137,000	385,000	320,000

^a Derived from a racemic polytertiary amine P(TDAE) polymerized with the 1 : 1.9 ZnEt₂/H₂O initiator system ($\eta_{sp}/c = 1.5 \text{ dl g}^{-1}$, $c = 0.5 \text{ g dl}^{-1}$ in water, H⁺ form).

^b Derived from an optically active P(TDAE)* polymerized with the 1 : 1.2 ZnEt₂/R(-) 3,3-dimethyl-1,2-butanediol initiator system ($\eta_{sp}/c = 37 \text{ dl g}^{-1}$, $c = 0.5 \text{ g dl}^{-1}$ in water, H⁺ form).

^c In salt-free water.

^d In 0.1 N KCl.

^e $c = 0.160 \text{ g dl}^{-1}$.

^f $c = 0.145 \text{ g dl}^{-1}$.

form was found to be *ca.* 4 times greater than the M_w in the H⁺ form thus explaining the higher viscosity in regard to Q-P(TDAE) 17 in the same form. Therefore, it is concluded that for Q-P(TDAE)'s with low X values, the organic micro-phase is composed of aggregates of several macromolecules. That Q-P(TDAE) are satisfactory models for Q-P(TBMAE) was checked by comparing the reduced viscosity of Q-P(TDAE) 17 with that of Q-P(TBMAE) 20 in salt-free water, both compounds being in the OH⁻ form. As expected, values of the same order of magnitude, $\eta_{sp}/c = 0.03$ ($c = 0.160 \text{ g dl}^{-1}$) and 0.06 ($c = 0.24 \text{ g dl}^{-1}$), were obtained respectively. These findings show that Q-P(TBMAE) and Q-P(TDAE) display similar acid-base properties when their quaternization states are comparable. Further, the higher hydrophobic character of Q-P(TBMAE) 7, compared to Q-P(TDAE) 17, pointed out before from a comparison of their potentiometric titration curves, is primarily due to a lower degree of quaternization rather than to a larger hydrophobicity of *N*-substituents.

Though, we have no experimental certitude, thus far, for the destabilisation of Q-P(TBMAE) 7 aggregates as pH decreases and β starts increasing, it is likely that the abnormal variation of η_{sp}/c with δ , in the range $0.07 < \delta < 0.25$ of the viscometric titration curve (Figure 1), results from such a destabilisation. Whatever is the mechanism of that destabilisation, one can conclude that the protonation of tertiary

amine residues of Q-P(TBMAE)_{RS}^{S*} 7 in the range $0.25 < \delta < 0.85$, *i.e.*, in the high buffering region, occurs through simultaneous cooperative chemical and conformational transitions as discussed in the case of Q-P(TDAE) 17.¹⁻³

Chiroptical Properties

Acid-base reactions on optically active macromolecules generally cause optical activity changes which can be regarded as resulting from conformational modifications or from chemical ones.⁶ In the case of poly(α -amino-acid)s, such optical activity changes are usually given in regard to pH and discussed in terms of conformation-dependence.^{7,8} This approach has been applied to Q-P(TBMAE)_{RS}^{S*} 7.

The plot in Figure 2 shows the variations of the optical rotatory power of Q-P(TBMAE)_{RS}^{S*} 7 *vs.* pH in water when going from the OH⁻ form to the H⁺ form by addition of hydrochloric acid. A drastic change in optical activity occurs when the constant pH value corresponds to the high buffering region of the potentiometric titration curve. A similar S-shaped curve is also observed for Q-P(TDAE)* 17, when the acid-induced optical rotation changes are plotted *vs.* pH (Figure 2). However, the same acid-induced changes have been reported as obeying a linear relationship when plotted *vs.* β , the degree of protonation of tertiary amino groups, *i.e.*, in regard to the chemical state of amine chromophores.³

In an attempt to correlate the changes in Q-

P(TBMAE)_{RS}^{S*} optical activity to acid-base reactions, as previously done for Q-P(TDAE), ORD, and CD data were plotted in regard to δ , ϵ , and β parameters in the following.

Figure 3 shows the ORD of Q-P(TBMAE)_{RS}^{S*} 7 in water for various values of the degree of neutralization δ . The complex positive ORD curve of the OH⁻ form ($\delta=0$) remained unchanged from $\delta=0$

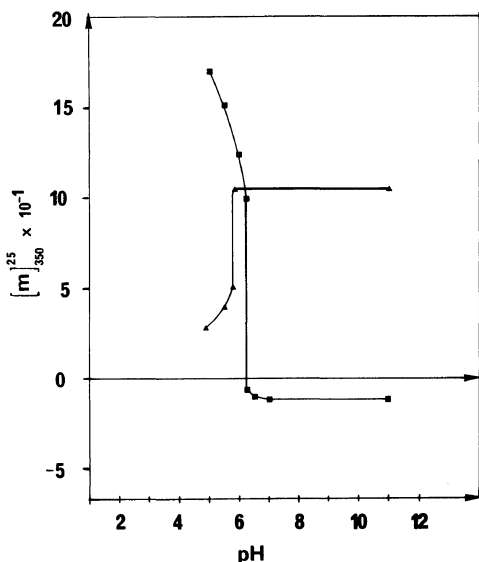


Figure 2. Variations in optical rotatory power [m] with pH for Q-P(TDAE)* 17 (—■—) and Q-P(TBMAE)_{RS}^{S*} 7 (—▲—) in water ($T_N=1 \times 10^{-2} \text{ mol l}^{-1}$).

to $\delta=0.4$ and then shifted down linearly to lower optical rotations as δ increased to 1, as shown in Figure 4 for $\lambda=350 \text{ nm}$. Considering the ϵ and β parameters, monomolar rotation [m], and monomolar ellipticity [θ] as well, were found constant in the $0 < \epsilon < 1$ range but varied linearly in the range $0 < \beta < 1$, in the case of Q-P(TDAE)* 17.³ Figure 4 shows that the acid-base induced changes in optical activity, as monitored by ORD, are not simply related to ϵ or β in the case of Q-P(TBMAE)_{RS}^{S*} 7. For comparison, acid-base induced optical activity changes were then monitored by CD.

Figure 5 shows the CD spectra of Q-P(TBMAE)_{RS}^{S*} 4 for various values of δ in water. The CD spectrum of Q-P(TBMAE)_{RS}^{S*} 4 (OH⁻ form) displays a large negative band centered at 219 nm. As with Q-P(TDAE)* 17,³ the CD spectrum of Q-P(TBMAE)_{RS}^{S*} 4 remained unchanged during the ion-exchange reaction at quaternary ammonium sites ($0 < \delta < 0.07$; $0 < \epsilon < 1$; $\beta=0$), but was drastically modified as soon as protonation occurred ($0.07 < \delta < 1$; $\epsilon=1$; $0 < \beta < 1$). The 219 nm CD bands decreased as δ increased to 1. For $\delta=\beta=1$, Q-P(TBMAE)* 4 took on its fully protonated form and the CD spectrum consisted of a weak negative CD band centered at 233 nm, and the beginning of a positive band located down in the inaccessible UV range.

The variation in molar ellipticity of Q-P(TBMAE)_{RS}^{S*} 4 at 219 nm in regard to ϵ and β , in water, is shown in Figure 6. In contrast to variations

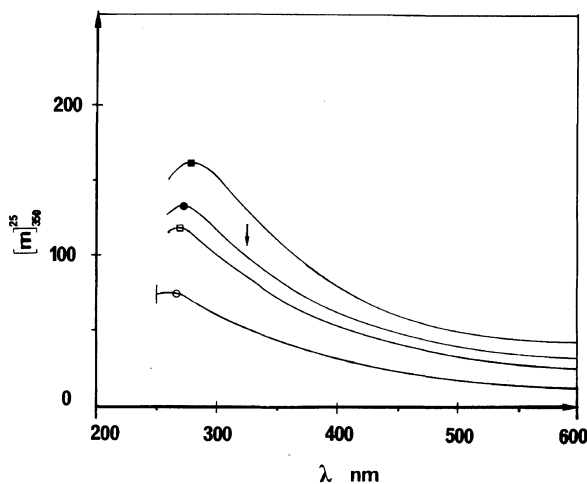


Figure 3. ORD spectra of Q-P(TBMAE)_{RS}^{S*} 7 ($T_N=1 \times 10^{-2} \text{ mol l}^{-1}$ in water) for various values of the overall degree of neutralization: $0 < \delta < 0.4$ (—■—); $\delta=0.6$ (—●—); $\delta=0.75$ (—□—); $\delta=1$ (—○—).

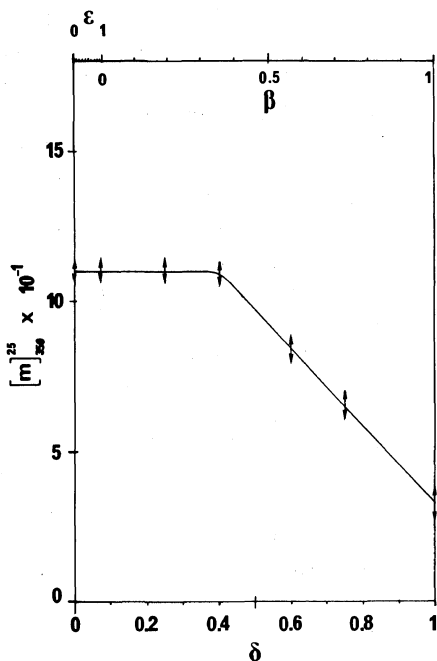


Figure 4. Polarimetric titration curve of Q-P(TBMAE)_{RS}^{S*} 7 ($T_N=1 \times 10^{-2} \text{ mol l}^{-1}$ in water) using HCl 1 M as the titrating reagent.

in optical rotation which not simply correlatable to ϵ and β , the ellipticity at 219 nm was independent of ϵ and varied quasi-linearly with β .

The discrepancies in the variations of ORD and CD in water in regard to ϵ and β (Figures 4 and 6) is still not well understood. The invariance of ORD, in a range where CD changed, cannot be assigned to the particular ionization behavior of Q-P(TBMAE)_{RS}^{S*} 4 in water since there is no obvious relation with the high buffering region of the potentiometric titration curve. It is likely that this invariance is related to the presence of aggregates. This interpretation is supported by the fact that, in the 80:20 v/v methanol-water mixture where Q-P(TBMAE) protonates conventionally without aggregation, optical rotatory power and ellipticity vary quasi-linearly as soon as β increases (Figure 6).

On the other hand, the acid-induced ORD and CD changes reported in Figures 4 and 6 cannot be simply related to the high buffering effect, since no particularity was detected at the limits, $\delta=\gamma_1=0.25$ and $\delta=\gamma_2=0.85$. Therefore, attempts were made to correlate these changes with the protonation reaction, as was done for Q-P(TDAE)*. For this

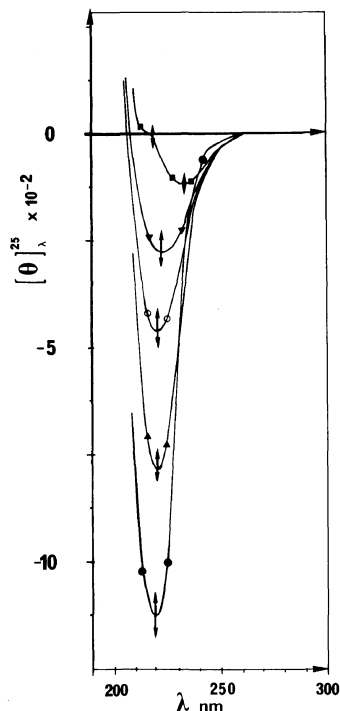


Figure 5. CD spectra of Q-P(TBMAE)_{RS}^{S*} 4 ($T_N=1 \times 10^{-2} \text{ mol l}^{-1}$ in water) for various values of δ : $0 < \delta < 0.004$ (—●—); $\delta=0.25$ (—▲—); $\delta=0.5$ (—○—); $\delta=0.6$ (—▼—); $\delta=1$ (—■—).

purpose, the origin of CD changes was considered.

The CD spectra of Q-P(TBMAE)_{RS}^{S*} 4 in the OH⁻ and H⁺ forms (shown in Figure 5 for $\delta=0$ and $\delta=1$, respectively) appear very similar to those already reported for P(TBMAE)_{RS}^{S*}, the non-quaternized precursor with a racemic main chain in dioxane (deprotonated form) and in water (H⁺ form), respectively.⁴ For P(TBMAE)_{RS}^{S*}, the negative CD band observed at 215 nm (deprotonated form), was assigned to the $n \rightarrow \sigma^*$ electronic transition of tertiary amine chromophores while the CD spectrum of the H⁺ form was considered to consist of thioether Cotton effects only; the involvement of nitrogen non-bonding electrons in a chemical bond with H⁺ ions result in the vanishing of the $n \rightarrow \sigma^*$ cotton effect in the CD spectrum of deprotonated P-(TBMAE)_{RS}^{S*}.⁴ The predominance of the nitrogen $n \rightarrow \sigma^*$ cotton effect in the CD spectrum of deprotonated P-(TBMAE)* was also shown from the study of the dissymmetric perturbation of nitrogen and sulfide chromophores by chiral centers present

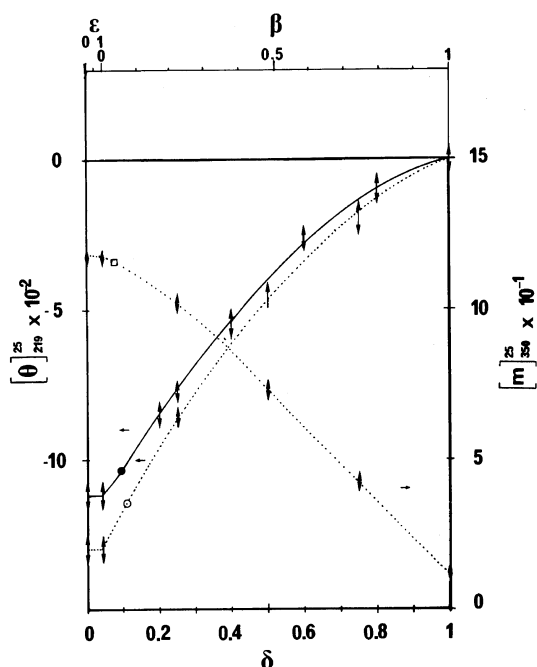


Figure 6. Dichrometric titration curves of Q-P(TBMAE)_{RS}* 4 in water (—●—) and in 80:20 v/v methanol–water (···○···) and its polarimetric titration curve in 80:20 v/v methanol–water (···□···) ($T_N = 1 \times 10^{-2} \text{ mol l}^{-1}$).

in each repeating unit.⁹

On the basis of these remarks and the similarities in the CD spectra of Q-P(TBMAE)_{RS}* 4 and of its precursor, P(TBMAE), in corresponding protonation states, it is concluded that the 219 nm negative CD band appearing in Q-P(TBMAE)_{RS}* 4 CD spectra is primarily due to the $n \rightarrow \sigma^*$ electronic transition of tertiary amine chromophores and reflects the protonation state of these weakly basic groups as in the case of P(TBMAE)_{RS}.

The slight deviation from linearity in the $[\theta] = f(\delta)$ curve in the $0 < \beta < 1$ range (Figure 6), in contrast to the linear variation observed for Q-P(TDAE)* 17, seems to be a general feature of optically active polyelectrolytes with chiral centers in side-chains and is assignable to the effects of chemically changing neighbors on specific chiroptical characteristics of repeating units as already discussed for various examples.¹⁰

In conclusion, Q-P(TBMAE) copolymers behave quite similarly to Q-P(TDAE) ones insofar as protonation is concerned. In the course of this work, it

was shown that slightly quaternized *N*-*s*-butyl-*N*-methyl ($X < 10$) and also *N,N*-diethyl compounds remain soluble in water but aggregate. This finding suggests the existence of a fifth domain in the diagram proposed to schematize the X -dependence of the solution behavior of Q-P(TDAE) during protonation.¹ This fifth domain, in which deprotonated macromolecules aggregate, constitutes a logical intermediate between the fully aggregated state of deprotonated non-quaternized P(TDAE) macromolecules which precipitate in water and the monomolecular globular state shown with $X = 17$ (ref 1 and this work). The exact determination of the limits of the new domain will require further investigation. However, it is possible to state that the cooperative transition reported for the first time for Q-P(TDAE), can be extended to other members of the series of poly[thio-1-(*N*-*s*-butyl-*N*-methylaminomethyl)ethylene]. Insofar as optical activity is concerned, it has been shown that acid-induced CD changes in Q-P(TBMAE) reflect the chemical state of amine side-chain groups through the $n \rightarrow \sigma^*$ Cotton effect of tertiary amine nitrogen chromophores, regardless of the medium, and of the cooperative conformational transition as evidenced by potentiometry and viscometry. The presence of configurationally enriched carbon atoms in the side-chains did not induce any particularity in the acid-base reactions or, in the chiroptical properties in Q-P(TBMAE) polydiastereoisomer with racemic main-chains. In particular, no phenomenon assignable to a stereo-ordered conformation was shown for the globular state.

REFERENCES

1. D. Vallin, J. Huguet, and M. Vert, *Polym. J.*, **12**, 113 (1980).
2. J. Huguet, *Nouv. J. Chimie*, **3**, 293 (1979).
3. D. Vallin, J. Huguet, and M. Vert, "Polymeric Amines and Ammonium Salts," IUPAC, E. J. Goethals, Ed., Pergamon Press Oxford, 1980, p 219.
4. J. Huguet and M. Vert, *Eur. Polym. J.*, **12**, 469 (1976).
5. C. Villiers and C. Braud, *Nouv. J. Chimie*, **2**, 33 (1978).
6. M. Vert, "Polyelectrolytes," E. Selegny, Ed., Reidel Publishers Co., Dordrecht, Holland, 1974, p 347.
7. P. Doty, A. Wada, J. T. Yang, and E. R. Blout, *J. Polym. Sci.*, **23**, 851 (1957).
8. G. D. Fasman, "Poly- α -Amino-Acids. Protein Models for Conformational Studies," G. D. Fasman,

- Ed., Marcel Dekker Inc., New York, 1967, p 499.
9. J. Huguet, M. Vert, M. Reyx, M. Sepulchre, and N. Spassky, *Polymer*, **20**, 961 (1979).
10. M. Vert, "Optically Active Polymers," E. Selegny, Ed., Reidel Publishers Co., Dordrecht, Holland, 1979, p 291.