dimensions.) A clue to the origin of this failure may lie in the observation that the extended Hückel[19] (quantum mechanical) map for alanine agrees rather closely with the semiempirical map, indicating that the quantum mechanical estimation of the conformational energy of peptides is sensitive to the particular molecular orbital method employed. Since it would be valuable to have a reliable quantum mechanical method for estimating the validity of, or for refining the parameters used in the semiempirical potential energy functions applied to polypeptides, a comparison and analysis of the assumptions adopted and the methods used in both the extended Hückel and PCILO molecular orbital calculations and their effects on the calculation of conformation dependent energies appears to be desirable.

Though the PCILO method goes beyond the SCF–MO–CNDO/2 molecular orbital scheme[39] by incorporating some electron correlation, the PCILO method involves the use of localized orbitals. To determine the importance of electron correlation and the use of localized orbitals to the calculated conformational energies, it becomes important to recalculate the alanine map using the SCF–MO–CNDO/2 method. The feasibility of such a calculation is presently under study.

Acknowledgment. The author is grateful to Dr. R. Ditchfield for several helpful conversations.

(39) J. A. Pople, *Accounts Chem. Res.*, 3, 217 (1970).

Living Poly(2-vinylquinoline)

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ABSTRACT: Living poly(2-vinylquinoline) was prepared. Its spectrum as well as the spectra of the dead polymer and of the monomer are reported. Conductance studies of the sodium salt of living poly(2-vinylquinoline) in THF showed that its dissociation is very low, $-\Delta H_{\text{diss}} = 2.3$ kcal/mol, $\Delta S_{\text{diss}} = -43$ eu. These findings resemble those previously reported for the living poly(2-vinylpyridine) and indicate that the cation associated with the growing end is simultaneously coordinated with the first quinoline moiety of the polymer. Kinetic studies led to the determination of the propagation constant $k_{\pm}$, its activation energy (7.9 kcal/mol), and the temperature-independent factor (9.6×10^8 M^{-1} sec^{-1}). The free $\sim\!\sim\text{VQ}^-$ carbanions seem to be not much more reactive than the ion pairs.

Pursuing our studies of anionic propagation, we investigated the kinetics of polymerization of living sodium 2-vinylquinoline in tetrahydrofuran.

Experimental Section

Preparation of 2-Vinylquinoline.[1] 2-(2-Hydroxyethyl)quinoline (19.9 g), 3.5 g of powdered KOH, and 0.1 g of *N*-phenyl-β-naphthylamine were slowly heated to 103° under a 12-mm vacuum. The monomer which distills over was fractionated *in vacuo;* the proper fraction was dried by stirring it for 4–5 days over CaH_2 and finally distilled under high vacuum into ampoules equipped with breakseals which eventually were sealed off.

The identity and purity of the monomer were established by gpc and nmr.

Preparation of Living Sodium Poly(2-vinylquinoline). The preparation of living poly(2-vinylquinoline) was accomplished in a high-vacuum system with break-seals instead of stopcocks, following the procedure described elsewhere.[2] Several initiators were used, namely, sodium naphthalene, the dianion of dimeric 1,1-diphenylethylene, α-methylstyrene tetramer, or metallic sodium. The preparations were performed at three different temperatures, *viz.*, −50, −20, and +20°. A four- to fivefold excess of the monomer was added to a stirred solution of the initiator in tetrahydrofuran (THF). The initiation was completed in a fraction of a second and the resulting living polymer appeared to be the same whatever method was used for its preparation. However, living polymer of low degree of polymerization, DP, rapidly "aged" when it was prepared and kept at room temperature, although the polymer was stable when prepared and kept at low temperature (<−20°). The aging manifested itself in spectral changes which could be noted after 2 hr of storage (see the next section).

Spectra of 2-Vinylquinoline and of the Living and Dead Poly(2-vinylquinoline). The spectrum of 2-vinylquinoline is depicted in Figure 1. Two sharp absorption maxima appear at 325 and 336 nm, the extinction coefficients being 5.1×10^3 and 3.14×10^3, respectively. The absorbance at 336 nm was utilized for monitoring the consumption of the monomer in kinetic experiments because the absorbence of the polymeric chain (excluding the contribution of the carbanions) is negligible at this wavelength. The dead polymer absorbs at shorter wavelengths (<330 nm), as shown in Figure 1. The sharp peak at 328 nm is attributed to the quinoline moiety; it also appears in the spectrum of the monomer albeit, as expected, at slightly longer wavelength.

The spectrum of the freshly prepared living poly(2-vinylquinoline) of DP >4 shows a broad maximum at 345 nm, ϵ 1.3×10^4 (see again Figure 1). At this wavelength the extinction coefficients of 2-vinylquinoline and of segments of poly(2-vinylquinoline) are 370 and 150, respectively. The concentration of living polymers before the addition of the monomer and after completion of the polymerization was determined by the optical density at 340–345 nm. Although the position of this flat maximum shifts slightly toward shorter wavelength (by 2–3 nm) as the DP of the polymer increases from 4 to 15, its extinction is hardly affected. Therefore, the determination of the concentration of the living polymer at the end of a run is not complicated by this shift.

Living poly(2-vinylquinoline) shows another broad absorption band at about 520 nm. The ratio of OD(520)/OD(345) ≈ 0.3; however, its value varies slightly in a haphazard way. The 520-nm absorption is sensitive to aging processes—the position of the maximum shifts considerably toward longer wavelength with time (within about a week) and the relevant optical density doubles. The aging only slightly changes the absorption in the 345-nm region; the maximum shifts toward a shorter wavelength, and this

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(1) G. B. Bachman and L. V. Heisey, *J. Amer. Chem. Soc.*, 70, 2378 (1948).

(2) M. Szwarc, "Carbanions, Living Polymers and Electron-transfer Processes," Interscience, New York, N. Y., 1968, Chapter IV.

TABLE I
CONDUCTANCE STUDIES OF LIVING POLY(2-VINYLQUINOLINE) IN THF

Temp, °C	Λ_0, cm^2/(ohm equiv)	$K_{diss}{}^a \times 10^9$, M
−70	15.0	33
−55	21.0	23
−40	27.0	16.2
−25	34.5	11.9
−10	43.0	9.0

^{a} K_{diss} = dissociation constant for $\sim\sim$VQ$^-$,Na$^+$ $\rightleftarrows$ $\sim\sim$VQ$^-$ + Na$^+$.

TABLE II
KINETICS OF PROPAGATION, $\sim\sim$VQ$^-$,Na$^+$ + VQ IN THF

Initiator^a	Temp, °C	[$\sim\sim$VQ$^-$,Na$^+$] $\times 10^5$ M	k_{obsd}, M^{-1} sec^{-1}
D$^-$,Na$^+$	−35	14.0	27.8
Q$^-$,Na$^+$	−35	10.1	29.0
D$^-$,Na$^+$	−35	4.62	29.4
Q$^-$,Na$^+$	−35	2.85	30.2
Q$^-$,Na$^+$	−35	1.96	28.0
D$^-$,Na$^+$	−20	15.5	128
D$^-$,Na$^+$	−20	7.42	128
D$^-$,Na$^+$	−20	7.22	121
Q$^-$,Na$^+$	−20	4.96	106
Q$^-$,Na$^+$	−20	2.50	121
D$^-$,Na$^+$	−20	2.30	121
Q$^-$,Na$^+$	−20	1.77	111
D$^-$,Na$^+$	−5	36.6	310
Q$^-$,Na$^+$	−5	4.34	306
D$^-$,Na$^+$	−5	2.65	304
Q$^-$,Na$^+$	−5	0.84	303
Q$^-$,Na$^+$	−5	0.43	305
D$^-$,Na$^+$	+9.5	9.70	604
Q$^-$,Na$^+$	+9.5	5.41	603
D$^-$,Na$^+$	+9.5	3.32	625
Q$^-$,Na$^+$	+9.5	2.55	624
Q$^-$,Na$^+$	+9.5	1.62	600

^{a} D$^-$,Na$^+$ initiated by the dianion of the dimeric 1,1-diphenylethylene. Q$^-$,Na$^+$ initiated by the preformed living polyvinylquinoline.

affects the minimum at about 330 nm; its depth becomes greatly reduced as the polymer ages.

No attempt was made to investigate the cause of the aging processes. We ascertained only that they are of no importance if a properly prepared living polymer is used in the kinetic studies within 2 hr after its preparation.

Conductance Studies. The conductance of living poly(2-vinylquinoline) was investigated in the device described elsewhere.[3] The concentration of the living polymer was varied from 7×10^{-5} to 3×10^{-6} M. The results are summarized in Table I, and the plot of log K_{diss} *vs.* $1/T$, shown in Figure 2, leads to $-\Delta H_{diss}$ = 2.3 kcal/mol and $\Delta S_{diss} = -43$ eu.

Kinetics of Propagation. Kinetics of propagation was followed spectrophotometrically by monitoring the absorbence at 336 nm (λ_{max} of 2-vinylquinoline). The technique described by Tölle, *et al.*,[4] was used in all the experiments. The concentrations of the living polymers and the respective bimolecular rate constants, k_{obsd}, are given in Table II. The initial concentrations of the monomer varied from $\sim 10^{-4}$ to 9×10^{-3} and of the living polymer from 0.4×10^{-5} to 36×10^{-5} M. In spite of variation by a factor of 100 in the concentration of living polymers, no variations in the rate constants of propagation were observed.

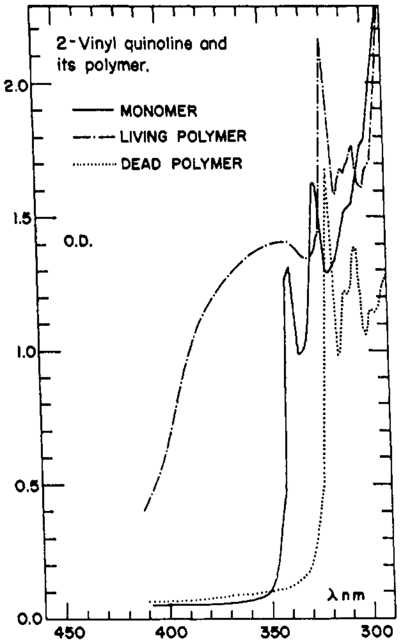

Fig.1

Figure 1. Spectrum of 2-vinylquinoline and living and dead poly-(2-vinylquinoline) in THF; arbitrary scale of OD's. The relative OD's of the different curves *do not give* the ratios of the respective extinction coefficients. The graphs resemble, however, the spectra obtained in actual kinetic experiments. For pertinent extinction coefficients, see the text.

Apparently the contribution of the free $\sim\sim$VQ$^-$ ions to the rate of propagation is negligible. The plot of log k_{obsd} *vs.* $1/T$ is shown in Figure 3. The activation energy of propagation is 7.9 kcal/mol, the temperature-independent factor being 9.6×10^8 M^{-1} sec^{-1}.

Discussion

The conductance studies demonstrate that $\sim\sim$VQ$^-$,Na$^+$ pairs are substantially less dissociated in THF than the sodium salt of living polystyrene.[4,5] Furthermore, the heat of dissociation of the former ion pairs is only −2.3 kcal/mol, *i.e.*, considerably less negative than that of the latter (−8.2 kcal/mol), the entropies of dissociation being −43 and −59 eu, respectively. These observations imply that the sodium cation of the living poly(2-vinylquinoline) pair is coordinated with the first quinoline moiety of the polymeric chain. Hence, the living poly(2-vinylquinoline) salt forms in THF the highly reactive loose pairs, while the bulk of sodium salt of living

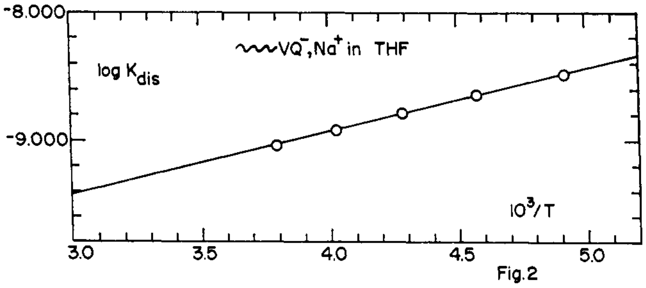

Fig.2

Figure 2. van't Hoff plot of dissociation constant of sodium salt of living 2-vinylquinoline in THF; $-\Delta H_{diss}$ = 2.3 kcal/mol, $\Delta S_{diss} = -43$ eu.

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(3) See ref 2, pp 273–287.

(4) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).

(5) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

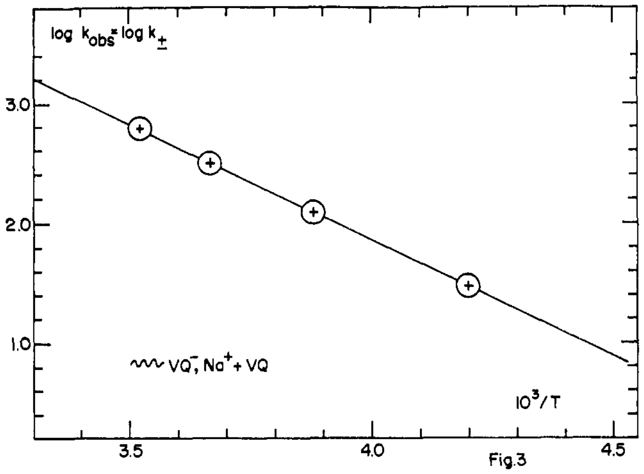

Figure 3. Arrhenius plot of propagation constant of sodium salt of living 2-vinylquinoline in THF; $E_{\pm} = 7.0$ kcal/mol, $A_{\pm} = 9.6 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$

polystyrene is in the form of unreactive tight pairs. A similar situation has been previously encountered in the course of studies of living poly(2-vinylpyridine) and discussed in the respective paper.[6] The K_{diss} values are higher by about a factor of 5 for the living polyvinylquinoline salt than for the polyvinylpyridine salt, although the heats of dissociation are similar.

The largest variation of [$\sim$VQ$^-$,Na$^+$] was attained in the kinetics runs performed at $-5°$, *viz.*, from 0.4×10^{-5} to 36×10^{-5} M (see Table II). Although the fraction of dissociation of $\sim$VQ$^-$,Na$^+$ pairs into free ions increased from *ca.* 0.4 to 4%, the rate constant of propagation remained virtually constant. Hence, the reactivity of the free $\sim$VQ$^-$ could not exceed that of the $\sim$VQ$^-$,Na$^+$ ion pairs by more than 30%, *i.e.*, $k_-/k_{\pm} < 1.3$. The observed propagation constant, k_{obsd}, is equal therefore to $k_{\pm}$, the propagation constant of the ion pairs.

The $k_{\pm}$ values of the propagation of $\sim$VQ$^-$,Na$^+$ and of the sodium salt of living polyvinylpyridine are remarkably similar. The relevant activation energies and temperature-independent factors are 7.9 kcal/mol ($A = 0.96 \times 10^9\ \mathrm{sec}^{-1}$) and 7.7 kcal/mol ($A = 1 \times 10^9$),[6] respectively. However, the significance of this fact is not clear, because the rates of addition of two *different* monomers to two *different* carbanions are compared. Nevertheless, these findings suggest that the rates of propagation of the respective free anions should be comparable also. According to Fisher and Szwarc,[6] the free anions of living poly(2-vinylpyridine) are much more reactive than the corresponding ion pairs, *i.e.*, in the pyridine system the ratio $k_-/k_{\pm}$ was claimed to be 50. The present work indicates that the $k_-/k_{\pm}$ ratio is less than 1.3 in the quinoline system. Closer examination of the data reported in ref 6 convinces us that the trends depicted in Figure 3 of the above reference were overemphasized. The variation of k_{obsd} with 1/[living polymers]$^{1/2}$ is small indeed, less than 10% in most cases, while the experimental scatter is substantial. It seems, therefore, that in the polyvinylpyridine system, like in the polyvinylquinoline system, the reactivity of free carbanions is comparable to that of ion pairs because the coordination of the cation with the nitrogen base loosens the pairs and makes them more reactive—a point previously elaborated by Fisher and Szwarc.[6]

Finally, it may be tempting to compare the systems living polyvinylquinoline and polyvinylpyridine with polyvinylnaphthalene and polystyrene. Unfortunately, kinetic studies of living polyvinylnaphthalene[7] were performed in those days when the distinction between the reactivities of free ions and ion pairs was not fully appreciated. Nevertheless, examination of the available data indicates that the rates of addition of vinylnaphthalene to its living polymers are comparable to the rates of addition of styrene to living polystyrene. In this respect the hydrocarbon systems and the heterocyclic systems seem to be similar.

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(6) M. Fisher and M. Szwarc, *Macromolecules*, **3**, 23 (1970).

(7) F. Bahsteter, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 3909 (1963).