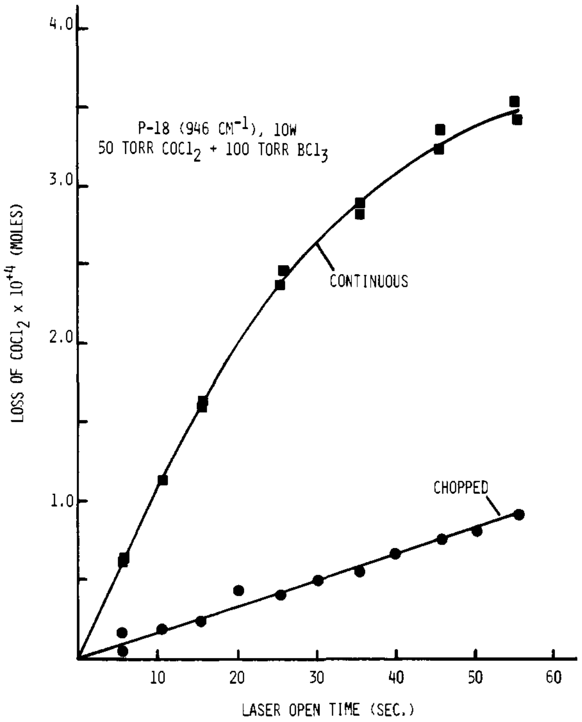

Figure 1. Phosgene decomposition vs. laser irradiation time for initial partial pressures of 100-torr BCl_3 and 50-torr phosgene. Power was 10 W and intensity 26 W/cm^2 with the P-18 (946 cm^{-1}) line. The upper curve is for a continuous beam, and the lower curve is for a chopped beam.

BCl_3 and subsequent vibrationally controlled chemical processes. The results may be interpreted in terms of a thermally derived process in which the reaction rate is dependent upon the temperature within the beam envelope. The temperature would be lower for the chopped conditions. In this particular system, BCl_3 probably exhibits additional specific catalytic activity because laser-phase homogeneous thermolysis of SF_6–$COCl_2$ mixtures has little or no effect on $COCl_2$ although high temperatures are produced.[4-6] These high temperatures would be accompanied by a corresponding vibrational distribution of molecular states. The thermal interpretation is also consistent with the findings of Meyer et al.,[9] who showed that $COCl_2$ was selectively decomposed in BCl_3 by an electrical discharge or radiofrequency excitation.

Bachmann et al.[4] attached special significance, in terms of a nonthermal mechanism, to the visible luminescence of BCl_3. We found this visually detected luminescence disappeared when the 10-W, 7-mm beam was chopped at 50 Hz. The luminescence reappeared when the chopper was slowed to about 10–13 Hz (~75–100-ms pulses). Interestingly, this pulse length corresponds to that found recently for a continuous polymer pulsing in SF_6–B_2H_6 mixtures.[8] Interpreting this luminescence as having a thermal origin under these conditions is consistent with the delayed luminescence found by Ambartzumian et al.[10] and Karlov et al.[11] in BCl_3 and the experiments of Houston et al.,[12] who attributed the major segment of a 50-μs infrared double-resonance absorption signal in BCl_3 to vibrational–translation relaxation.

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Electric-Field Orientation of Poly(α-L-glutamic acid) in Various Conformations as Studied by Reversing-Pulse Electric Birefringence

Sir:

We wish to report the usefulness of the reversing-pulse electric birefringence (RPEB) technique, introduced by O'Konski and co-workers[1-3] and formulated by Tinoco and Yamaoka,[4] to the understanding of the electric-field orientation of poly(α-L-glutamic acid), $(Glu)_n$, to which the contribution of counterions is expected.[5] In dimethylformamide (DMF), the un-ionized $(Glu)_n$ helix possesses a large intrinsic permanent electric dipole moment along the symmetry axis (μ_3) in addition to an atomic and electronic polarizability anisotropy ($\Delta\alpha = \alpha_{33} - \alpha_{11}$);[6] hence, it can be oriented by an external electric field.[6,7] However, the orientation mechanism of $(Glu)_n$ would be complex in a salt-free aqueous solution in which the side-chain carboxylates are ionized and the conformation varies with pH. Besides μ_3 and $\Delta\alpha$,[8] there will be field-induced dipole moments due to the counterion fluctuation[9] or the ionic atmosphere polarization.[10] A suggestion was made that the permanent dipole moment of $(Glu)_n$ is largely suppressed by a time-dependent polarizability at higher ionizations of the side-chain carboxylates.[9] Thus, a direct proof of the role of counterions on the $(Glu)_n$ surface should assist understanding of the polyelectrolyte behavior of biopolymers.

Theoretical calculations have illustrated that an RPEB signal (Δn) should display an extremum (Δ_m) after a lapse of time (t_m) upon the reversal of an applied pulse field if a molecule has both μ_3 and $\Delta\alpha$; the depth depends on the ratio of $\mu_3^2/kT\Delta\alpha$ (Figure 1 of ref 4). If a polyion has no μ_3, a similar extremum still appears due to a time-dependent polarizability when the mobility of counterions on the polyion surface is slow; the depth depends on the ratio of the relaxation time of the counterion redistribution (τ_3) to that of the molecular rotation of the polyion (τ_1) (Figure 4 of ref 4). In either case, the extremum is undetectable if $\mu_3 \ll \Delta\alpha$ or $\tau_3 \ll \tau_1$. It should be pointed out that the Δ_m, which would be otherwise observed for a polyion such as $(Glu)_n$ with an appreciable μ_3, becomes undetectable if the counterion mobility is much faster than the molecular rotation and if the fast-induced dipole moment is much larger than μ_3.

Figure 1 shows oscillograms of the RPEB signal of $(Glu)_n$ and the applied pulse field in DMF and in aqueous solutions in the pH range where $(Glu)_n$ undergoes a helix–coil transition. A deep minimum ($\mu_3^2/kT\Delta\alpha$ ca. 2)[4] appears expectedly in the DMF solution where $(Glu)_n$ is in the helix formation (a). In aqueous solutions, the minimum tends to be shallower with an increase of pH. At pH 4.17 (b), where $(Glu)_n$ is a complete helix showing the largest negative molar rotation, the depth is shallow as compared with that in DMF. This is a strong indication that counterion-induced dipole moments partially suppress the contribution of μ_3 to the field orientation. At pH 5.09 (c), where the helical content is usually assumed to be 100%, the minimum disappears completely. In the pH range 5.3–5.8 (d), where $(Glu)_n$ begins to change from helix to coil, the RPEB signal is complicated, showing a maximum after the pulse reversal. In the middle of

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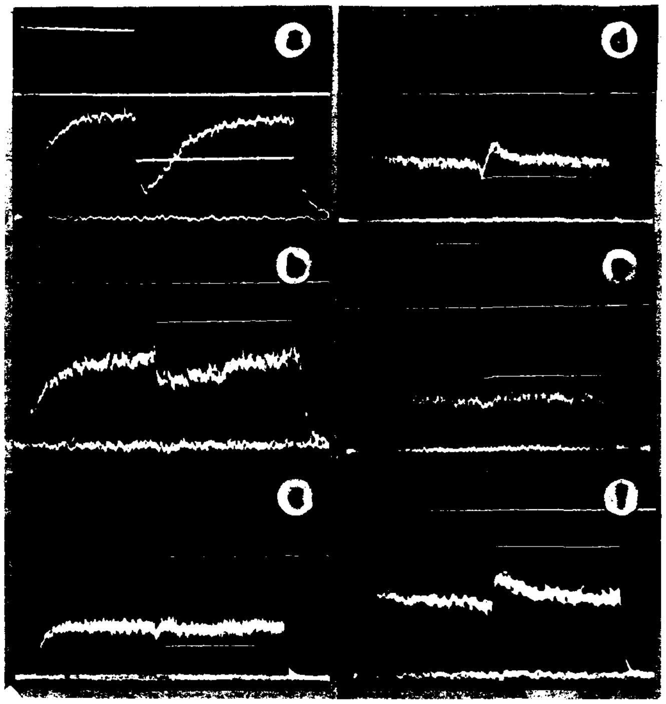

Figure 1. Oscillograms of the RPEB signals of (Glu)$_n$ and the applied-pulse electric field at 20 °C and at 535 nm (a) and 500 nm (b–f). The sign of the RPEB signal was positive. The concentrations of (Glu)$_n$ in mM are (a) 4.9 and (b–f) ca. 1.0. The pH, the degree of neutralization, and the molar rotation at 233 nm in 10 deg cm^2 mol^{-1} are (b) 4.17, 0.10, and -1.95×10^4; (c) 5.09, 0.25, and -1.89×10^4; (d) 5.74, 0.40, and -1.75×10^4; (e) 6.33, 0.60, and -6.58×10^3; and (f) 7.02, 0.92, and -2.30×10^3. The pH was adjusted by addition of 20 mM NaOH to the salt-free (Glu)$_n$ solution which had been dialyzed at a pH of 3.86. The electric-field strength in kV/cm and the sweep time in µs/division are (a) 6.4 and 100, (b) 5.6 and 50, (c) 7.5 and 50, (d) 7.0 and 50, (e) 5.9 and 50, and (f) 5.9 and 50. The Kerr law was obeyed in a low-field range up to ca. 6 kV/cm in each (Glu)$_n$ solution.

the transition (pH 6.0–6.4), the RPEB signal again shows neither minimum nor maximum (e). As (Glu)$_n$ is fully ionized (pH >7), the RPEB signal shows a peculiar shape, i.e., a maximum with application of a normal square pulse and another much larger one for a reversed pulse (f). The electric-field strength neither affected nor altered the general pattern of the RPEB signal appreciably at each pH, but the concentration of the counterion Na$^+$ did influence the pattern.

The Δ_m at low pHs (<3.9) became pronounced and closer to that in DMF. This indicates that the contribution to field orientation from the counterion-induced dipole is less effective, probably because the side-chain carboxylates are mostly un-ionized and the mobility of tightly bound protons is low compared with the rotational diffusion of the whole (Glu)$_n$ molecule ($\tau_3/\tau_1 \gg 1$). As the ionization proceeds, the counterion-induced dipole dominates over the permanent dipole, and the mobility of the counterions (mostly Na$^+$) on the helical (Glu)$_n$ is very fast ($\tau_3/\tau_1 \ll 1$); hence, almost no minimum appears in the RPEB signal. The RPEB result is direct evidence which supports the importance of the counterion-induced dipole in the electric-field orientation of an ionized polymer with intrinsically dipolar structure. The fully ionized (Glu)$_n$ can be oriented by electric field (f). This result suggests that the (Glu)$_n$ is not in the shrunken, random-coil form but rather an extended stiff coil in salt-free solutions. The RPEB pattern (f) is reproducible and dependent on field strengths to some extent and reveals a close similarity with a theoretical curve in which the transverse permanent dipole moment μ_1 contributes to the orientation ($\beta < 0$ in Figure 2 of ref 4).

In conclusion, the orientation mechanism of (Glu)$_n$ in aqueous solutions appears to involve all of the permanent dipole moment (the longitudinal and transverse components), the fast and slow counterion-induced dipole moments, and the covalent polarizability, depending on the various conformations of (Glu)$_n$. The RPEB method[1-4] is thus shown to be powerful and applicable to the study of the behavior of counterions on the polyelectrolyte surface in aqueous solutions.

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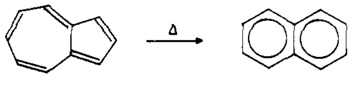
Azulene–Naphthalene Rearrangement. Involvement of 1-Phenylbuten-3-ynes and 4-Phenyl-1,3-butadienylidene[1]

Sir:

The thermal rearrangement of azulene (**1**) to naphthalene (**2**) was discovered in 1947.[2] Yet, the mechanism of this reaction



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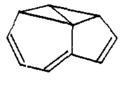

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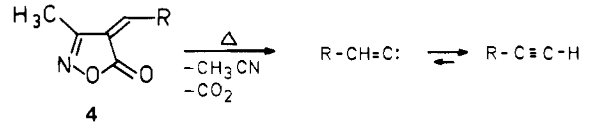
is still a matter for speculation. Scott and Agopian[3] suggested that the 1,2 carbon scrambling observed by pyrolysis of naphthalene at 1035 °C (contact time 11 s) was due to the reversible formation of azulene via the tetracyclic triene **3**. Alder et al.[4] have demonstrated that the azulene–naphthalene rearrangement under static conditions (440 °C; 2–5.5 h) is catalyzed by radicals. Furthermore, substituted and labeled azulenes give as major products naphthalenes with retention of substituent and label position, but in addition, products of apparent substituent or label migration as well as substituent loss are obtained.[5,6] Two competing mechanisms based on rearrangements in azulene radical adducts have been put forward to explain the results.[6]

We now wish to report (i) a new mechanism which contributes to the azulene–naphthalene rearrangement, (ii) carbon scrambling in azulene itself both thermally and photochemically, and (iii) evidence that the reaction is not wholly unimolecular, even under flash vacuum pyrolysis conditions.

We have previously shown[7] that 4-alkylideneisoxazol-5-(4*H*)-ones (**4**) fragment thermally to vinylidenes,[8] the latter rearranging to acetylenes in high yields. Using labeled acetylenes, Brown et al.[9,10] demonstrated that the latter rearrangement is reversible.



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