gineering Research Council for support. Professor J. A. Koningstein has aided us in laser experimentation. Professor V. Balzani kindly supplied an advance copy of ref 6.

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Ordered Structure in Dilute Solutions of Ionic Biopolymers. 1. Preliminary Small-Angle X-ray Scattering Study of Aqueous Solutions of Sodium Polyacrylate[1]

Sir:

In 1965[2] we measured directly for the first time the mean activity coefficient (γ) of a polyelectrolyte and found that

$$\log \gamma = a + bm^{1/3} \qquad (1)$$

a, b are constants and m is polyelectrolyte concentration was valid for a variety of synthetic polyelectrolytes. On the basis of the interpretation advanced by Frank and Thompson,[3] the cube-root dependence was taken as suggesting that a more or less regular lattice-like ionic distribution exists in the solutions as a result of intermacroion linkage through the intermediary of counterions. In addition to the well-known low intensity of scattered light from the salt-free polyelectrolyte solutions,[4] the following experimental supports for such an ordered structure have recently been documented: the catastrophic change of the diffusion coefficient with salt concentration observed by the dynamic light scattering[5] for poly-L-lysine and the presence of the peak in the scattered intensity of neutron beam at small angles for sodium polyacrylate.[6-7] In this report, we describe a new evidence obtained by small-angle X-ray scattering.

Polyacrylic acid (PAA) of Wako Chemical Co., Osaka, was carefully fractionated into nine fractions by using 1,4-dioxane and n-heptane as solvent and precipitant, respectively.[8] The fractionated sample was purified carefully by ion exchange and repeated precipitation and finally freeze dried. The degree of neutralization was adjusted by addition of a NaOH solution. The water for solution preparation was purified first by ion exchange and subsequently by distillation from a quartz vessel under nitrogen atmosphere, in order to remove ionic impurities, which were supposed to vitiate the ordered distribution. The X-ray source was a Rigaku RU-200A (60 kV, 200 mA) and the scattered intensity of the Cu Kα X-ray was measured by using a position-sensitive proportional counter. Refer to a previous publication for a detailed description.[9] All measurements were made with a point-focussing camera system. The solutions were put in a compartment between two parallel mica films (1 or 2 mm apart). The scattering intensities both from solution and solvent were corrected for their respective absorptions.

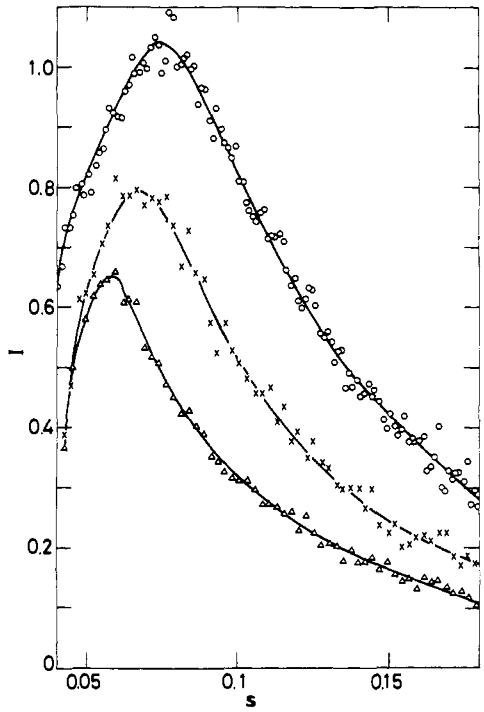

Figure 1. Scattered intensity vs. scattering vector plots for sodium polyacrylate solutions at 25 °C (weight-average degree of polymerization = 1020, degree of neutralization = 0.4): ○, 0.03 g/mL; ×, 0.02; △, 0.013.

Figure 1 shows the scattered intensity as a function of the scattering vectors **s** ($|\mathbf{s}| = 4\pi \sin \theta/\lambda$, where λ and 2θ are the wavelength of the X-ray used and the scattering angle, respectively) for a PAA sample ($\bar{P}w = 1020$) at three concentrations. It is clearly seen that the intensity I has a peak in the small angle region. The scattering peak was observed even at a low degree of neutralization, i.e., $\alpha = 0.1$, though the scattering curve is not given here. Although rather astonishing, this finding is consistent with the previously observed fact that the cube-root relation held also for polyions of a low charge density.[10] However, no peak was observed for polyacrylic acid at $\alpha = 0$.

When estimated by the Bragg relation ($2D_{\text{exp}} = 2\pi/\mathbf{s}_{\text{m}}$, where $\mathbf{s}_{\text{m}}$ is the **s** value at the peak), the dimension of the repeating unit of ordered structure ($2D_{\text{exp}}$) was fairly large (70–130 Å). It is most tempting to suggest that such a large distance is due to a regular distribution of the macroions. The next question is the mode of the distribution. Although the argument cannot be conclusive at present, there might be two asymmetric lattice structures for fully stretched rod-like macroions, namely the lattice proposed by Lifson and Katchalsky (L-K)[11] and hexagonal one.[12] The intermacroion distance calculated by the two models[13] was found to be smaller than, though fairly close to, $2D_{\text{exp}}$. This may suggest that the asymmetric lattice-like distribution is highly plausible. However, when the macroions are not fully extended as under our experimental condition, the hexagonal lattice dimensions would become larger. The computed minimum intermacroion distances for the symmetrical structures, i.e., simple cubic, body-centered cubic, and face-centered cubic, with the same density of macroions were much larger than $2D_{\text{exp}}$, suggesting that the symmetrical structures might be less important.

The decreasing tendency of $2D_{\text{exp}}$ with increasing concentration (c) at a fixed degree of neutralization (α) would be readily accepted. Further, $2D_{\text{exp}}$ was found to decrease with increasing α at a fixed c, which was surprising at a first glance, but might indicate that the ordered distribution is not due to "repulsion" between the macroions as claimed often,[4] but due

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to intermacroion "attraction" caused by the counterion-macroion attraction as suggested by us.[2,10]

Finally we note the close similarity in the distributions in macroion systems and electrically charged monodisperse latex particle systems. For the latter, Hachisu et al.[14] demonstrated unequivocally the presence of fluctuating hexagonal or cubic ordered structure in solutions. Such an ordered structure we certainly be of the great significance for solution properties of not only synthetic polyelectrolytes but also ionic biopolymers in general. Further study is in progress.

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References and Notes

(1) It would be fair to mention that an exploratory work of the small-angle X-ray study of polyelectrolyte solutions was carried out by I. Sakurada, Y. Nukushina, and N. Ise in 1958, though the results were unpublished. The recent remarkable development in the X-ray technique activated the long-dormant interest.
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(13) The theoretical distance $2D_{th}$ was obtained by the following relation, $2D_{th} = 2(w/\pi N_A lc)^{1/2}$ and $2D_{th} = (2w/N_A lc \sin 60°)^{1/2}$ for the L-K and hexagonal lattice models, respectively, where c is the polyelectrolyte concentration in grams/milliliter, w and l are the weight and length of the monomeric unit, and N_A is the Avogadro number.
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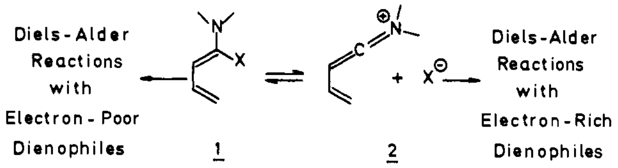
Diels–Alder Reactions of "Pull–Push" Activated Isoprenes

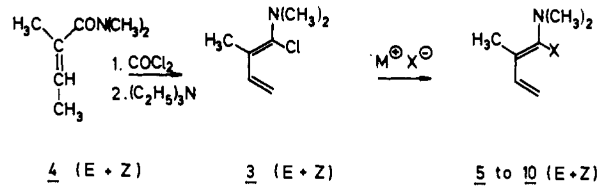
Sir:

1,1-Diheterosubstituted dienes have received only recently the degree of attention commensurate with their potentialities for the construction of highly functionalized rings by Diels–Alder cycloadditions. Such dienes are formally derived from vinylketenes which are too unstable and not accessible enough to be used successfully in Diels–Alder reactions.[1] The recently prepared vinylketenimines show a greater thermal stability and readily cycloadd to active dienophiles.[2] Vinylketene acetals[3-5] and thioacetals[6] have also been utilized as vinylketene equivalents in cycloaddition but were shown to react only with the most reactive dienophiles. However, the presence of an additional alkoxy or trimethylsilyloxy group at position 3 of the diene was found[4,7,8] to promote the reaction with less reactive dienophiles. 3-Hydroxy-2-pyrone has also been proposed[9] as a dienyl vinylketene equivalent, but its utility will probably be limited by the high temperatures (or pressures) required for the reactions with the less reactive dienophiles,

Scheme I. General Principle



Scheme II. Synthesis of 1,4 "Pull–Push" Isoprenes



We reasoned that 1-amino-1-heterosubstituted dienes **1** should meet the requirements for a useful class of vinylketene equivalents (Scheme I),

The presence of an electron-donating amino group at C-1 should confer high reactivity and orientational selectivity on dienes **1** in their reactions with electron-poor dienophiles. In addition, our previous studies on α-haloenamines[10] suggested that **1** could readily equilibrate with a vinylketeniminium salt **2** provided that X is a suitable leaving group. Diene **2** would be expected to undergo Diels–Alder reactions with electron-rich dienophiles. Clearly, a proper choice of the basic strength of the amine substituent should enable control of both the electrophilic character at C-1 and the nucleophilic character at C-4 (1,4 pull-push character), whereas variation of X should permit selective control of each of these properties.[11]

This proposition has been reduced to practice. 1-Chloro-1-dimethylaminoisoprene (**3**) was readily prepared from *N,N*-dimethyltiglic or angelic amide (**4**) (Scheme II). Phosgene (10 mL, 0.14 mol) was added at −10 °C to a solution of **4** (12.7 g, 0.1 mol) in dry CH_2Cl_2 (100 mL). After 24 h at 20 °C, followed by removal of the solvent and excess of $COCl_2$ in vacuo (caution: no moisture!), the residue was redissolved in CH_2Cl_2 (final volume, ±50 mL). Triethylamine (21 mL) was added dropwise at −10 °C. Additional stirring (1 h) at 20 °C, addition of petroleum ether (100 mL, bp 70–100 °C), filtration under N_2, and distillation gave 11.6 g (80%) of diene **3** as a thermally stable but readily hydrolyzable liquid, bp 55 °C (12 mm), consisting of a mixture of *E* and *Z* isomers. NMR, δ_{CCl_4} (Me_4Si) major isomer, 7.00 (dd), 5.13 and 5.00 (dd + dd), 2.50 (s), 1.86 (s); minor isomer, 6.86 (dd), 5.23 and 5.13 (dd + dd), 2.50 (s), 1.91 (s) ($J_{gem} = 1.5$, $J_{cis} = 12$, $J_{trans} = 20$ Hz).

Compound **3**[12] behaved as methylvinylketeniminium chloride and displayed a high reactivity toward nucleophilic reagents. This provided a simple and practical route toward a series of activated isoprenes,[13,14] **5–10** (Table I).

The high electrophilic character of diene **3** is illustrated by its capacity of undergoing Diels–Alder reactions with unactivated nitriles (Scheme III). Thus, refluxing **3** (2 mmol) for 3 days in 5 mL of acetonitrile, followed by addition of triethylamine, yields 60% aminopyridine **11a**: NMR δ_{CCl_4} (Me_4Si) 2.2 (br s, 3 H), 2.3 (s, 3 H), 2.8 (s, 6 H), 6.5 (d, 1 H), 7.1 (d, 1 H). In the presence of KI, the cycloaddition occurred in 3 h. This clearly indicates that the reactive species adding across the C≡N bond is a vinylketeniminium chloride or iodide in equilibrium with **3** or, in the presence of KI, with **6** formed in situ. More interesting to us was the remarkable chemoselec-

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