

## Electrostatic persistence length and its relation to a unified theory of polyelectrolytes in solution

The concept of an electrostatic persistence length<sup>1-4</sup> can lead to a unified theory of polyelectrolytes in solution with and without added salt. The bewildering variety of different models<sup>5-13</sup> which has been employed until now, can be explained on the basis of one model: the wormlike chain having homogeneous charge density with a potential of mean force between charges given by a Debye-Hückel potential. The object of this Letter is to discuss these assertions and to provide a simple generalization for the results of refs 1-4.

### Model

The polyelectrolyte of contour length  $l$  in a solution with dielectric permittivity  $D$  is approximated by a continuous space curve:

$$\vec{r}(s) \quad (0 \leq s \leq l)$$

having a uniform charge density equal to

$$qN/l\xi$$

where  $q$  is the elementary charge,  $\xi$  is the charge density parameter and  $N$  is the number of charges on the polyelectrolyte. The non-divergent free energy of curvature  $F$  of the polyelectrolyte consists of a non-electrostatic part  $\Delta F_t$  and an electrostatic term  $\Delta V_{el}$ :

$$F[\vec{r}(s)] = \Delta F_t + \Delta V_{el}$$

$$= \int_0^l ds \left[ \frac{1}{2} k_B T L_p \vec{\rho}^2 + \frac{q^2}{\xi^2 D} \times \int_s^l dt \left( \frac{\exp -\kappa |\vec{r}(t) - \vec{r}(s)|}{|\vec{r}(t) - \vec{r}(s)|} - \frac{\exp -\kappa(t-s)}{(t-s)} \right) \right] \quad (1)$$

where the curvature vector  $\vec{\rho} = \partial^2 \vec{r} / \partial s^2$ ,  $k_B$  is Boltzmann's constant,  $T$  is the temperature,  $\kappa^{-1}$  is the Debye-Hückel shielding length,  $L_p$  is the bare persis-

tence length and  $A = lN^{-1}$ . In ref 2 it is shown that a term  $\Delta V_1$  analogous to  $\Delta F_t$  can be extracted from  $\Delta V_{el}$  in a consistent manner:

$$\Delta V_1 = \int_0^l ds \frac{1}{2} k_B T L_e \vec{\rho}^2 \quad (2)$$

with the electrostatic persistence length to first order given by ref 1:

$$L_e = Q/4\kappa^2 A^2 \xi^2 \quad (3)$$

provided the total persistence length

$$L_T = L_p + L_e \gg \kappa^{-1} \quad (4)$$

(Bjerrum length  $Q = q^2/Dk_B T$ ). Hence the polyelectrolyte can be viewed as a wormlike chain with persistence length  $L_T$ , perturbed by an excluded-volume effect  $\Delta V_{el} - \Delta V_1$ .

### Derived models: with added salt

*Counterion condensation.* If

$$L_p > A^2 \xi^2 Q^{-1} \quad (5)$$

then, from elementary algebra,

$$L_T > \kappa^{-1} \quad (6)$$

for all  $\kappa^{-1}$ . If  $n$  is the concentration of added monovalent salt,

$$\kappa^2 = 8\pi Qn \quad (7)$$

Since  $L_T$  is a correlation length expressing the extension of rigidity along the chain, charges near the polyelectrolyte are influenced by an almost cylindrically symmetrical charge distribution provided equation (5) is satisfied. Hence, the counterion condensation theory is valid<sup>6-10</sup>:

$$\xi = 1 \quad \text{for } A > Q \quad (8)$$

$$\xi = Q/A \quad \text{for } A \leq Q \quad (9)$$

In that event, equation (5) can be replaced by equations (10) and (11):

$$L_p > A^2 Q^{-1} \quad \text{for } A > Q \quad (10)$$

$$L_p > Q \quad \text{for } A \leq Q \quad (11)$$

Equations (10) and (11) provide lower bounds for the validity of the cylindrical models. As  $Q \approx 7 \text{ \AA}$  for H<sub>2</sub>O and  $L_p \geq 10 \text{ \AA}$  for most polyelectrolytes, equations (10) and (11) are almost always satisfied and, usually,  $L_T \kappa \gg 1$ .

*Excluded volume theory.* See ref 2. The main features are: firstly, expansion of the polyelectrolyte caused by an increase in  $L_T$  because of the enlargement of the Debye-Hückel radius, and by excluded-volume effects; secondly, for  $\kappa^{-1} > (2QL_p)^{1/2}$ ,  $L_T$  becomes so large that the excluded volume decreases.

*Polyelectrolytes near the rod limit.* For chains with  $l = O(L_T)$  excluded-volume effects are negligible and the polyelectrolyte is a wormlike chain with persistence length  $L_T^{-1}(\Delta V_{el} - \Delta V_1)$  tends to zero).

### Derived models: without added salt

*Counterion condensation.* Let us assume that screening arises from the uncondensed, monovalent counterions ( $I = \text{total concentration}$ )<sup>4</sup>. Then:

$$\kappa^2 = 4\pi Q\xi^{-1} I \quad (12)$$

and usually  $L_e \gg L_p$ , therefore

$$L_T \approx L_p = Q/4\kappa^2 A^2 \xi^2 \quad (13)$$

Assuming  $\xi = O(1)$ , we can easily see that  $L_T \kappa \gg 1$ , since  $8\pi^{1/2} \xi^{-1/2} I^{1/2} A^2 Q^{-1/2} \ll 1$  is invariably satisfied. Further discussion is analogous to that for counterion condensation with added salt.

*Excluded-volume theory.* We replace equation (7) by equation (12), and an analogous theory results. For a large number of cases, excluded-volume effects can be neglected. However, we must ensure that the polyelectrolyte coils do not entangle.

*Polyelectrolytes near the rod limit.* Again, excluded-volume effects are negligible for  $l = O(L_T)$ .

Polyelectrolytes with  $k = 0(1)$ .

According to ref 1, the polyelectrolyte is virtually a rigid rod because the persistence length is given by:

$$L_T = \frac{QN^2}{72\xi^2} + L_p \quad (14)$$

### Conclusions

If the Debye-Hückel screening length is well defined by equations (7) and (12), a versatile picture presents itself of polyelectrolyte behaviour at any salt concentration. Incorporated in a consistent manner are: counterion condensation; excluded-volume effects; enlargement of the total persistence length up to and beyond the contour length.

Some remaining problems may be mentioned: (a) a rigorous derivation of the Debye-Hückel potential of mean force for all concentrations of added salt; (b) deviations from Manning's limiting laws when  $L_p$  is not large enough to ensure  $L_T \kappa \gg 1$ <sup>14</sup>;

(c) calculation of  $L_e$  to second order; generalization for non-wormlike chains; (d) polyion-polyion interactions<sup>13</sup>; a rigorous derivation of the excluded volume, perhaps including dispersion forces caused by fluctuations in the counterion atmosphere of the polyelectrolyte; (e) possible role of short range forces of non-Coulombic origin.

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## Decomposition of benzoyl peroxide in the presence of poly(*N*-vinyl carbazole), poly(*p*-methoxystyrene) and some model compounds

Benzoyl peroxide (BPO) is effective for initiating the polymerization of *N*-vinyl carbazole (VCZ) at 60°C but the reaction does not have the characteristics of a radical process; it appears that initiation results from interaction between the monomer and the initiator<sup>1-3</sup>. The corresponding polymerization of *p*-methoxystyrene (MOS) also shows special features<sup>4</sup>; they are explicable in terms of pronounced transfer to BPO, a process properly regarded as induced decomposition of the initiator. It is relevant that tertiary amine groups are present in VCZ and its polymer, and ether groups in MOS and its polymer; these groups are known to have substantial effects upon the decomposition of BPO<sup>5</sup>. An examination was therefore made of the decomposition of BPO in the presence of polyVCZ, polyMOS, *N*-ethyl carbazole (ECZ) or *p*-ethyl anisole (EAN); ECZ and EAN can be taken as model compounds for the polymers. The samples of polymers had been prepared by radical polymerization in benzene solution using azoisobutyronitrile as initiator.

BPO labelled in its carbonyl groups with <sup>14</sup>C was used at a concentration of 0.5 g/dm<sup>3</sup> in benzene. Reaction

mixtures were degassed and kept for various periods at 60°C before isotope dilution analysis for carbon dioxide and, in some cases, benzoic acid<sup>6</sup>. Figure 1 shows that ECZ suppressed the formation of carbon dioxide but the decrease in yield was matched by an increase in that of benzoic acid. It should be noted that the apparent yields of the acid may include contributions corresponding to other substances readily exchanging C<sub>6</sub>H<sub>5</sub>COO with the acid. Figure 2 shows that ECZ and polyVCZ depressed the yield of carbon dioxide and markedly reduced *t*<sub>1/2</sub> for decomposition of the peroxide. EAN produced effects similar to those produced by ECZ. The influence of polyMOS was much smaller than those of either the model compound EAN or polyVCZ. Figure 2 shows also that polystyrene and poly(methyl methacrylate) produced no significant effects upon the rate of decomposition of BPO in benzene or upon the yields of carbon dioxide.

Gel permeation chromatography was used to examine polyVCZ for changes caused by treatment with BPO in solution. Chloroform was used as eluent and narrow-distribution samples of poly-

styrene as standards. For estimation of  $\bar{M}_n$  and  $\bar{M}_w$ , the *Q*-factor method was applied with values of 41 and 76 for *Q* for polystyrene and polyVCZ, respectively<sup>7</sup>. The values of molecular weights for samples of VCZ are not exact and are used for comparative purposes only. Table 1 shows that  $\bar{M}_n$  passed through a minimum during the treatment and that  $\bar{M}_w$  increased markedly, apparently towards a limiting value; appreciable changes occurred even after decomposition of the peroxide was virtually complete according to results shown in Figure 2. Labelled

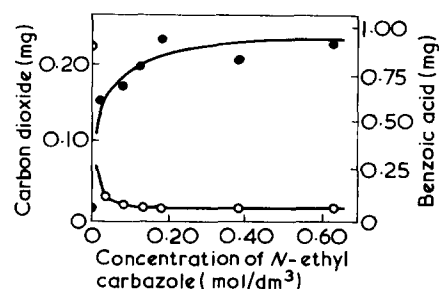


Figure 1 Effect of *N*-ethyl carbazole on products of the decomposition at 60°C for 120 h of 1 mg of benzoyl peroxide in 2 cm<sup>3</sup> benzene: ○, carbon dioxide; ●, benzoic acid