with the data obtained from $(VA_3)_n$ and $(V_2A_2)_n$ and possibly $(VA)_n$.

This polar pleated sheet structure has already been described, however, without reference to the original work of Pauling and Corey, for a sheet structure called "βDL" obtained on a low molecular weight sample of (γ-benzyl-D,L-glutamate)$_n$.[8] This βDL conformation was suggested on the basis of a value of the chain repeat unit c between 0.52 and 0.56 nm estimated from X-ray and density measurements.

The proposal of the polar pleated sheet structure for $(VA_3)_n$, $(V_2A_2)_n$, and (γ-benzyl-D,L-glutamate)$_n$, however, raises questions concerning the positions of the infrared absorption bands. Indeed, the spectra are very similar to those found for the usual cross-β structures of the pleated sheet type with an antiparallel arrangement of the chains for all-L polypeptides, although the conformational states of the residues are very different in the two structures. Theoretical analysis may help to elucidate this question.

References and Notes

(1) Urry, D. W. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 672–6.
(2) Urry, D. W.; Goodall, M. C.; Glickson, J. D.; Mayers, D. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1907–11.
(3) Veatch, W. R.; Fossel, E. T.; Blout, E. R. *Biochemistry* **1974**, *13*, 5249–56.
(4) Heitz, F.; Lotz, B.; Spach, G. *J. Mol. Biol.* **1975**, *92*, 1–13.
(5) Lotz, B.; Colonna-Cesari, F.; Heitz, F.; Spach, G. *J. Mol. Biol.* **1976**, *106*, 915–42.
(6) Heitz, F.; Lotz, B.; Dêtriché, G.; Spach, G. *Biochim. Biophys. Acta* **1980**, *596*, 137–40.
(7) Haydon, D. A.; Urban, B. W.; Heitz, F.; Spach, G. Proceedings of the International Symposium on Biomolecular Structures, Conformation, Function and Evolution, Madras, 1978, in press.
(8) Lotz, B.; Heitz, F.; Spach, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, *276*, 1715–8.
(9) Heitz, F.; Lotz, B.; Colonna-Cesari, F.; Spach, G. In ref 7.
(10) Pauling, L.; Corey, R. B. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 251–6.
(11) Pauling, L.; Corey, R. B. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 729–40.
(12) Hesselink, F. T.; Scheraga, H. A. *Macromolecules* **1972**, *5*, 455–63.
(13) Miller, W. G.; Brant, D. A.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 67–80.
(14) De Santis, P.; Morosetti, S.; Rizzo, R. *Macromolecules* **1974**, *7*, 52–8.
(15) Ramachandran, G. N.; Chandrasekaran, R. *Indian J. Biochem. Biophys.* **1972**, *9*, 1–11.
(16) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *45*, 2091–2101.
(17) Nêmethy, G. *Ann. N.Y. Acad. Sci.* **1969**, *155*, 492–506.
(18) Trudelle, Y. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1001–5.
(19) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308–13.
(20) Ascoli, F.; De Angelis, G.; Del Bianco, F.; De Santis, P. *Biopolymers* **1975**, *14*, 1109–14.
(21) Lotz, B.; Keith, H. D. *J. Mol. Biol.* **1971**, *61*, 201–15.

Expansion of Long Polyions in Simple Salt Solutions

D. M. Soumpasis* and K. H. Bennemann

Institute for Theoretical Physics, Freie Universität Berlin, 1000 Berlin 33, Arnimallee 3, West Germany. *Received August 1, 1980*

ABSTRACT: Using simple theoretical arguments, the results of Monte Carlo work on off-lattice chains with excluded volume, and published light scattering data of polyion expansion in the dilute regime, it is found that for degrees of polymerization $N \gtrsim 10^3$, the electrostatic expansion factor α_s obeys a general asymptotic relation of the form $\alpha_s = f(\xi,\chi^*)N^{g(\xi,\chi^*)}$, where ξ and χ^* are natural parameters describing the polyion charge density and salt-screening effects, respectively. In contradiction to existing theories that predict $g(\xi,\chi^*) = \text{const} \approx {}^1/_{10}$, the behavior of g and f is found to be very complex. There is evidence that for $\xi > 1$, both f and g become independent of ξ as may be predicted by Manning's limiting laws for polyelectrolytes.

Introduction

A rigorous ab initio treatment of the expansion of polyion chains in salt solution amounts to dealing with a system of N particles, interacting via screened electrostatic interactions and subject to the constraint of being connected into a chain. Due to these three aspects the problem is extremely difficult to handle and no satisfactory solution exists to date. Quite recently, the problem has been attacked by Richmond[1] and Bailey,[2] who used a Gaussian chain model and the self-consistent field (SCF) approach introduced by Edwards[3] and subsequently discussed, refined, and extended by de Gennes,[4] Reiss,[5] and Yamakawa,[6-8] as well as by Odijk and Houwaart[9] and Fixman and Skolnick,[10] who adopted a wormlike model for the polyion and studied the electrostatic excluded-volume effect, explicitly taking into consideration local chain stiffening. In this work we adopt a completely different approach. We avoid mathematical complexities as far as possible and try to understand the basic features of the problem, using a combination of general theoretical arguments, our present state of knowledge of the excluded-volume problem in general, and last but not least a rather extensive analysis of available experimental data of polyion expansion. It is our opinion that, due to the complexity of the problem at hand, real progress toward a quantitative theory cannot be achieved unless at least the qualitative aspects are understood and taken into consideration.

Apart from its attractiveness per se, the polyion expansion problem can serve as a particularly convenient model for the excluded-volume problem in general, since in this case the relevant monomer–monomer interactions are well-defined and may be generally described in terms of a few natural parameters. It is therefore hoped that its study will also contribute toward a better understanding of the excluded-volume effect of real polymers in solution.

Electrostatic Expansion Factor

Consider a chain of N monovalent charged sites joined by $N - 1$ bonds of length a immersed in a 1:1 electrolyte solution with n ions per unit volume and a dielectric constant ϵ at temperature T. Introducing the mean-square radius of gyration[7]

$$\langle S^2 \rangle = \frac{1}{2N^2} \sum_i \sum_j \langle R_{ij}{}^2 \rangle \qquad (1)$$

where R_{ij} denotes the distance between sites i and j, we characterize the expansion of the chain due to the elec-

0024-9297/81/2214-0050$01.00/0 © 1981 American Chemical Society

trostatic forces[11] by means of the expansion factor

$$\alpha_s = (\langle S^2\rangle/\langle S^2\rangle_0)^{1/2} \tag{2}$$

where

$$\langle S^2\rangle_0 = (a^2/6)N \tag{3}$$

is the form obtained in the absence of any interaction among the monomers. Now the averages $\langle R_{ij}{}^2\rangle$ on the right-hand side of eq 1 are given by

$$\langle R_{ij}{}^2\rangle = \int \vec{R}_{ij}{}^2 \, \mathrm{d}\vec{R}_{ij} \int ... \int P(\vec{R}_i...\vec{R}_N)\, \delta[\vec{R}_{ij} - (\vec{R}_i - \vec{R}_j)]\, \mathrm{d}\vec{R}_1...\mathrm{d}\vec{R}_N \tag{4}$$

where $P(\vec{R}_i...\vec{R}_N)$, the probability density for the chain configuration $\{\vec{R}_1...\vec{R}_N\}$, obeys[7]

$$P(\vec{R}_i...\vec{R}_N) = Z^{-1}P_0(\vec{R}_i...\vec{R}_N)\exp[-(\beta/2)\sum_{\substack{ij\\ i\neq j}} W(R_{ij})]$$

$$Z = \int ... \int P_0(\vec{R}_i...\vec{R}_N)\exp[-(\beta/2)\sum_{\substack{ij\\ i\neq j}} W(R_{ij})]\ \mathrm{d}\vec{R}_i...\mathrm{d}\vec{R}_N \tag{5}$$

$$R_{ij} = |\vec{R}_i - \vec{R}_j|$$

$P_0(\vec{R}_1,...,\vec{R}_N,N,a)$ is the configurational probability density in the absence of interactions. It is well approximated by a multivariate Guassian form.[7]

$W(R_{ij})$ denotes the effective interaction (potential of mean force) between monomers i and j when all positions of the counterions and coions are canonically averaged with the chain configuration fixed. Quite generally one expects that $W(R_{ij})$ has the form

$$W(R_{ij}) = -\frac{e^2}{\epsilon R_{ij}}\varphi(\kappa^* R_{ij}) \tag{6}$$

$$\kappa^* = \kappa\psi(\kappa d) \qquad \kappa^2 = 8\pi\frac{e^2}{\epsilon k_B T}n_s$$

where n_s is the salt concentration, κ is the well-known Debye–Hückel parameter, d is the range of ionic hard-core repulsion, and $(\kappa^*)^{-1}$ is the effective screening length. $\varphi(\kappa^* R_{ij})$ describes the modification of the Coulombic interaction due to the screening effects of the mobile ions, and $\psi(\kappa d)$ the modification of the Debye–Hückel parameter due to hard-core effects (ionic size) that are expected to become significant at higher salt concentrations. For $\kappa \to 0$ one obtains the well-known exact limiting results $\kappa^* = \kappa$ and $\psi(x) = \exp(-x)$ of the Debye–Hückel theory.

Now mere inspection of eq 6–1 reveals that the expansion factor α_s can only depend on N, a, κ^*, and the Bjerrum length $\lambda = e^2/\epsilon k_B T$. Recalling that α_s is by definition dimensionless, simple dimensional reasoning leads us to the general form

$$\alpha_s = \alpha_s(N,\lambda/a,\kappa^* a) = \alpha_s(N,\xi,\chi^*) \tag{7}$$

It is seen that the expansion is most conveniently described in terms of the natural parameters N, ξ, and χ^*. The so-called charge density parameter ξ is the fundamental parameter of Manning's theory[12,13] for colligative properties of polyelectrolyte solutions and χ^* is the relevant measure of solvent screening effects in the case of a polyion which is a system of charges connected into a chain.

Exactly the same type of argument applies also in the case of the end-to-end distance expansion factor α_R[7] and leads to a relation analogous to (7).

Let us now recall some of the basic features of Manning's limiting theory for colligative properties. When ξ (determined from the chemical structure of the chain and λ) is *smaller than 1*, all small ions form a diffuse cloud around the macroion and are treated in the Debye–Hückel approximation. When $\xi > 1$, a fraction $(1 - \xi^{-1})$ of the counterions "condenses" on the chain and reduces the structural value ξ to the effective value $\xi_{\text{eff}} = 1$. The rest of the small ions are again treated in Debye–Hückel approximation. Application of these concepts to relation (7) leads to

$$\alpha_s{}^u = \alpha_s(N,\xi,\chi) \qquad (\xi < 1) \tag{8}$$

and

$$\alpha_s{}^c = \alpha_s(N,\chi_c) \qquad (\xi > 1) \tag{9}$$

where $\chi = \kappa a$ and $\chi_c = \kappa\lambda$. In other words *if* Manning's basic concepts mentioned above are valid for polyion expansion too, one should find that in the case of highly charged polyions ($\xi > 1$) the expansion factor α_s (or equivalently the radius of gyration) *is independent of* ξ, *and screening effects are characterized by the same parameter* $\chi_c = \kappa\lambda$ *for all high charge density chains.* Manning's theory is of the limiting-law type; therefore this behavior should be observed exactly at limiting and approximately at moderate ionic strengths. Since we are primarily interested in long polymers, we now have to establish the form eq 7 takes in the region of large N. Analysis of the work done to date on the so-called excluded-volume problem clearly indicates two possibilities. The first is

$$\alpha_s = f(\xi,\chi^*)N^{\nu} \tag{10}$$

where ν *is a constant close to the Flory value* $^1/_{10}$. This form is suggested by Flory's well-known theory,[7,14,15] the general SCF approach[3,16] and extensive numerical work on the self-avoiding walk (SAW) problem *on lattices* using direct enumeration,[17] and Monte Carlo[18,19] techniques. Finally eq 10 is also suggested by the exact renormalization group (RG) treatment of the SAW-lattice problem by de Gennes.[20] In fact, if (10) applies to our problem, ν is known very precisely. According to the refined RG calculation of le Guillou and Zinn–Justin[21] it has the value 0.088 ± 0.001! For large N, Flory's classical result[7,14] takes the form

$$\alpha_s \sim z^{1/5} \tag{11}$$

where z is the so-called excluded-volume parameter

$$z = \left(\frac{3}{2\pi}\right)^{3/2}\frac{\gamma}{a^3}N^{1/2} \tag{12}$$

and γ is the "excluded volume" (binary cluster integral).[7] Now all four treatments of the electrostatic excluded volume mentioned above (ref 1, 2, 9, and 10) yield results of the Flory type (described by eq 11 and 12), which is a special case of eq 10. They share in common the $N^{1/10}$ dependence and the use of Debye–Hückel potentials to calculate γ. However, Richmond[1] and Bailey[2] calculate γ for *point particles*, while Odijk and Houwaart[9] and Fixman and Skolnick[10] consider local chain stiffening explicity and calculate γ for *rods* of length ≈ persistence length after determining the latter as a function of κ and λ by elasticity arguments plus Debye–Hückel approximation. We now introduce the second possibility, namely

$$\alpha_s = f(\xi,\chi^*)N^{g(\xi,\chi^*)} \tag{13}$$

i.e., now both the prefactor and the *exponent depend on the parameters determining the interactions among the monomers.* Theoretical justification for such a type of relation stems from Monte Carlo studies of Smith and

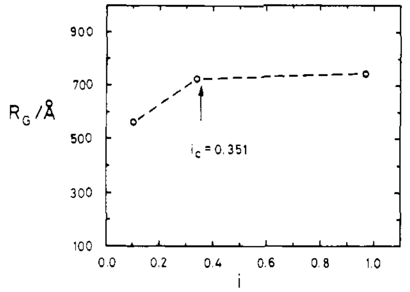

Figure 1. Radius of gyration R_G as a function of the degree of ionization i ($i \sim \xi$). Data of ref 27, NaPAA in 0.1 M NaCl, mol wt 4.8×10^5; assumed dependence: $i_c = 0.351$ corresponds to $\xi = 1$.

Flemming[22] and Flemming.[23] These authors studied the configurations of chains of *hard spheres* (diameter d, bond length a) in *real space* (i.e., not on lattices). They find that the expansion coefficients obey power laws with respect to N, but *both the exponent and the prefactor depend on the ratio d/a* (i.e., on the interactions). Since the polymer model studied in this work represents a real polymer much better than the SAW-lattice model or the Flory "monomer cloud" model we feel that relation 13 should be discussed on an equal footing with (10) although its analytical justification is not possible yet. However, the physical meaning of a relation of type 13 is quite clear. The expansion of any long albeit finite polymer may be thought to involve two basic mechanisms: (a) local chain stiffening (caused by the interactions of monomers with *small* "chain distance", i.e., distance *along* the chain) and (b) "excluded-volume effect" (caused by the interactions of monomers with *large* chain distance). Mechanism a causes "renormalization" of the bond length a expressed by the prefactor f in eq 13 while b causes a "renormalization" of the Gaussian exponent $^1/_2$, expressed by g. However, a and b work in *opposite directions*; i.e., very stiff chains have small excluded-volume effects and vice versa. Therefore if f is a function of the interaction parameters, g should be a function of them too and this is expressed in (13).

Analysis of Experimental Data

In order to check the simple ideas developed above one obviously has to analyze experimental data of the expansion of long polyions of *varying charge density* in a *wide range of ionic strengths*. However, a survey of published work indicates that this is not as straightforward as one may think simply because until now, no experiment has been specifically designed to examine the aspects we are interested in. Very often the number of experimental points is too small to draw graphs of reasonable precision and care must be taken to ensure that only data of *dilute* solutions are used since, due to the relatively high expansions involved, chain overlap may occur. A solution may be called dilute whenever the polymer concentration c_p does not exceed the threshold

$$c^* = M/R_G{}^3 \tag{14}$$

where $R_G = \langle S^2 \rangle^{1/2}$ denotes the measured radius of gyration and M the molecular weight of the sample. It is known[24] that interesting crossover phenomena occur upon going from the dilute ($c_p < c^*$) to the semidilute ($c_p \gtrsim c^*$) regime, which, in the case of polyions, have been recently discussed theoretically by Odijk.[25] However, we have to avoid such effects because we are interested in *isolated* chain behavior. Typically c_p is of the order 10^{-2} g·cm^{-3} and the experiments suggest that long-chain behavior is well established for $N > 10^3$. Therefore only data conforming to the conditions $c_p < 10^{-2}$ g·cm^{-3} and $N > 10^3$ are analyzed below.[26]

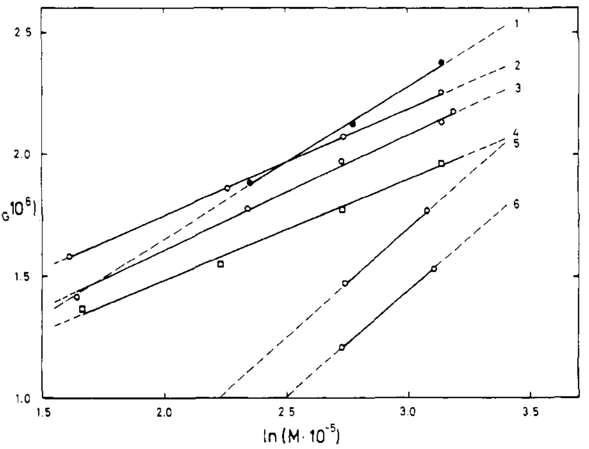

Figure 2. Molecular weight dependence of the radius of gyration at different ionic strengths. Data of ref 28 (NaPSS–NaCl). Salt concentrations: (1) 0.02 M; (2) 0.05 M; (3) 0.1 M; (4) 0.5 M; (5) 1.0 M; (6) 2.0 M. (R_G in cm.)

Figure 1 gives us an idea about the dependence of chain expansion on the charge density parameter (the degree of ionization i is proportional to ξ: $\xi = i\lambda/a$). The system studied[27] is NaPAA of mol wt 4.8×10^5 in 0.1 M NaCl. We were not able to find more than these three points, which is very frustrating considering the importance of this dependence for understanding polyion expansion and clearly more experimental data are badly needed. Nevertheless, this experiment of Orofino and Flory indicates that very probably, above $i_c = 0.351$ which *corresponds to* $\xi = 1$, the critical value for condensation, *the expansion becomes independent* (*or at least very weakly dependent*) *of polyion charge density*, as predicted by the analysis presented above (see eq 9).

Figure 2 shows log–log plots of the dependence of R_G on molecular weight in a wide range of ionic strengths and constant charge density for the system NaPSS (sodium poly(styrenesulfonate)) in NaCl solutions, based on experimental data of Takahashi, Kato, and Nagasawa.[28] The curves obtained are good straight lines (with correlation coefficient >0.99), which shows that R_G (i.e., α_s also) depends on M (or N) via a power law. However, *both the exponent and the prefactor are found to be functions of the ionic concentration.* In other words, the data are not described by a Flory-type relation such as eq 10 but by the more general form (13). The same conclusion may also be drawn from the analysis of data of Fisher, Sochor, and Tan,[29] who studied a different system, namely, NaPAMS (sodium poly[2-(acrylamido)-2-methylpropanesulfonate])–NaCl. As a matter of fact, as far as we can judge from the data available to us,[28-33] the behavior observed in the case of NaPSS is typical for flexible polyions in general, provided that the expansion is predominantly caused by electrostatic forces.

Using the data of the NaPSS–NaCl system,[28] we may now determine both the prefactor f and the exponent g entering eq 13 as functions of the screening parameter $\chi_c = \kappa\lambda$ (a = 2.5 Å for this polyion, corresponding to $\xi = 2.86$; i.e., condensation occurs in this case). The results are plotted in Figures 3 and 4. Although one definitely needs more points in order to establish the form of the curves precisely, these graphs indicate that the dependence of both quantities on the screening parameter is rather complex and cannot be explained by existing theories. In accordance with the conjecture made at the end of the preceding section, it can be seen that local chain stiffening,

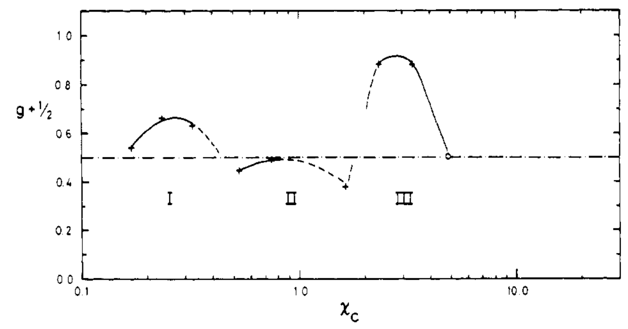

Figure 3. Dependence of the exponent g of eq 13 on the screening parameter $\chi_c = \kappa\lambda$: (–•–) Gaussian behavior; (- - -) assumed dependence; (O) Θ solvent (4.17 M NaCl, 25 °C).[28]

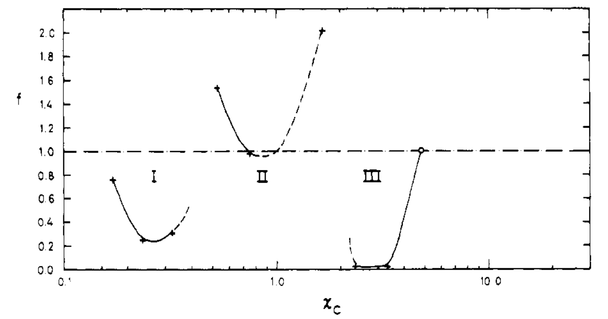

Figure 4. Dependence of the prefactor f of eq 13 on the screening parameter $\chi_c = \kappa\lambda$: (–•–) Gaussian behavior; (- - -) assumed dependence; (O) Θ solvent (4.17 M NaCl, 25 °C).[28]

as expressed by f, varies in opposite direction to excluded-volume effects (expressed by g), maxima of g corresponding to minima of f. Furthermore, it may be inferred that f and g behave in a qualitatively similar way in each of the three regions marked I, II, and III, corresponding to *low* (<0.05 M), *intermediate* (0.05–0.5 M), and *high* (>0.5 M) salt concentrations, and that probably *several* Θ *solvents* (*characterized by* $g = 0$, $f = 1$) *exist for this system*.[34]

As already mentioned in the preceding section, one expects that at higher ionic concentration specific ionic effects may become important. That this is indeed the case is shown in Figure 5. log–log plots of R_G vs. M for the systems NaPSS–NaCl[28] and KPSS–KCl[30] (salt concentration 0.5 M) reveal that upon replacing Na^+ by K^+ the exponent $g + {}^1/_2$ changes by almost a factor 2 (0.377 for Na^+, 0.625 for K^+).

We expect that these effects will become progressively smaller at lower ionic concentration but we did not find enough data to check this expectation. On the other hand, we find that differences in the chemical structure of the polyion backbone of $\xi > 1$ polyions do not affect the expansion unless other interactions (e.g., hydrophobic and hydrogen bonding interactions) become important. This statement is based on the analysis of data for NaPSS,[28] NaPAMS,[29] and NaPMOS (sodium poly[3-[(methacryloyl)oxy]propanesulfonate])[33] in NaCl buffers and KPSS,[30] PMPyTSO, and PMAMTSO[32] (see ref 32 for abbreviations) in KCl buffers.

Discussion

The main conclusions of this study may be summarized as follows:

(a) The expansion factor α_s of long polyions is most naturally expressed in terms of the parameters N, ξ, and χ^* (or χ) and is found to obey a relation of the form (13)

$$\alpha_s = f(\xi,\chi^*)N^{g(\xi,\chi^*)}$$

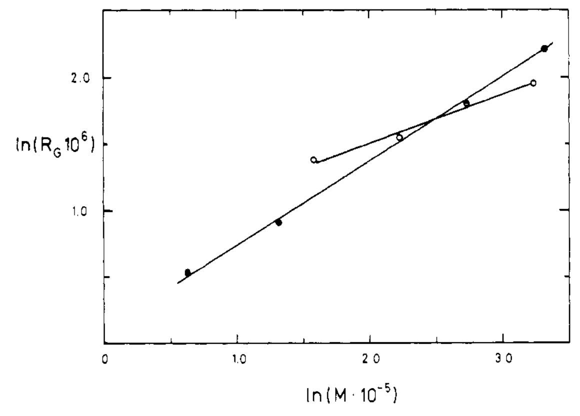

Figure 5. Dependence of the expansion on specific ionic effects. Salt concentration 0.5 M. (O) NaPSS–NaCl (ref 28); (●) KPSS–KCl (ref 30). (R_G in cm.)

(b) In the case of highly charged chains ($\xi > 1$) both f and g seem to become independent of charge density, being functions of the screening parameters $\chi^*_c = \kappa^*_c$ (or $\kappa_c = \kappa\lambda$) only.

(c) The experimental data indicate that the functions f and g are highly structured, exhibiting several extremes and vary in opposite directions. Furthermore it seems that $f = f[g(\xi,\chi^*)]$; i.e., the two functions are not linearly independent.

(d) At higher ionic concentrations specific ionic effects become important; it is possible that they may be adequately described by using the modified inverse screening length κ^* instead of the standard Debye–Hückel parameter κ to characterize the screening power of the solvent. (A statistical mechanical calculation of κ^* will be published elsewhere.)

(e) All existing theories of the electrostatic excluded-volume effect yield α_s expressions of the Flory type and are therefore incapable of describing the experimental data.

In connection with a it is interesting to note that a similar empirical power law is very commonly used to describe viscosity data in experimental publications. One has

$$\eta = KM^{\nu'} \tag{15}$$

where η is the intrinsic viscosity and K and ν' (the so-called Mark–Houwink parameters) are found to be salt dependent. Although the viscosity problem is more complicated due to the presence of both excluded volume and hydrodynamic interactions, a similar analysis applies to it as well and will be published in the near future.

In connection with b it must be stressed that a detailed experimental study of the dependence of the expansion on the charge density parameter will both elucidate this important aspect of the problem at hand and provide us with badly needed direct information on the counterion condensation phenomenon.

In connection with d we find that the specific ion effect demonstrated is surprisingly large (compare Figure 5) and, since the two measurements have been performed in different laboratories, could partly stem from differences in apparatus or data evaluation procedures. More experiments and a quantitative theoretical assessment of the importance of ionic hard-core and hydration effects are needed to clarify the situation. However, it should be noted that rather strong specific ionic effects (at slightly higher concentrations) have been also reported earlier in an extensive viscosity study of DNA–alkali metal halide solutions by Scruggs and Ross.[35]

All our arguments until now pertain to *long flexible* polyions (i.e., polymers with negligible inherent stiffness in the uncharged state). In order to extend the discussion to *long stiff* polyions as well, we now consider a polymer of contour length L and *nonelectrostatic* persistence length L_p, bearing N charges a distance a from each other. In the uncharged state and for $L \gg L_p$ this polymer may be represented by an equivalent Gaussian chain, of $\tilde{N} = L/2L_p$ Kuhn statistical segments of length $\tilde{a} = 2L_p$. Equation 3 becomes then

$$\langle S^2 \rangle_0 = (^1\!/_6\tilde{a})L \tag{16}$$

The charge density parameter ξ remains the same as before, and the parameter describing solvent screening $\chi^* = \kappa^* a$ becomes $\tilde{\chi}^* = \kappa^* \tilde{a} = 2\kappa^* L_p$. Reasoning in the same fashion as above leads us to an asymptotic relation of the same formal structure as eq 13, namely

$$\alpha_s = \tilde{f}(\xi,\chi^*)\tilde{N}^{\tilde{g}(\xi,\tilde{\chi}^*)} \tag{17}$$

However, the statements following eq 8 and 9 must be modified. For $\xi > 1$, we still expect that the expansion becomes independent (or very weakly dependent) of ξ but the salt dependence is governed by $\tilde{\chi}_c = \kappa 2L_p$ instead of $\chi_c = \kappa\lambda$. In other words, the salt-dependence curve of highly charged polyions of the same length is not universal anymore but depends on their elastic properties through L_p.

Futhermore, the functions of $\tilde{f}$ and $\tilde{g}$ will be different from f and g since now the Kuhn segments themselves and not merely their joints are charged. As mentioned above, this local stiffening effect has already been discussed in the theories of Odijk and Houwaart[9] and Fixman and Skolnick,[10] of course, within the limitations of the Flory approach, which always predicts $\tilde{g}$ = constant.

We hope that the findings presented herein demonstrate the necessity of a complete reconsideration of the polyion expansion problem both from the theoretical and from the experimental side and may serve as starting points for future quantitative work.

Acknowledgment. This work was completed while D.S. was visiting The Weizmann Institute of Science. Thanks is due Professors J. Schlessinger, A. Silberberg, and S. Lifson for their warm hospitality and many stimulating discussions. We also express our thanks to Professors Manning, Odijk, Fixman, and Bailey for sending us preprints of their work and the Deutsche Forschungsgemeinschaft and EMBO for financial assistance of D.S. through research grants.

References and Notes

(1) Richmond, P. *J.* Phys. *A* **1973**, *6*, L109.
(2) Bailey, J. M. *Macromolecules* **1977**, *10*, 725.
(3) Edwards, S. F. *Proc. Phys. Soc. London* **1965**, *85*, 613.
(4) de Gennes, P. G. *Rep. Prog. Phys.* **1969**, *32*, 187.
(5) Reiss, H. *J. Chem. Phys.* **1967**, *47*, 186.
(6) Yamakawa, H. *J. Chem. Phys.* **1968**, *48*, 3845.
(7) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(8) Yamakawa, H. *J. Chem. Phys.* **1971**, *54*, 2484.
(9) Odijk, T.; Houwaart, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
(10) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
(11) Throughout this work we discuss only the effects of electrostatic forces. Furthermore, we prefer to characterize the expansion by means of the radius of gyration $R_G = \langle S^2 \rangle^{1/2}$ and α_s, instead of using the end-to-end distance $\langle R^2 \rangle^{1/2}$ or α_R because the former quantities are the ones directly determined by light scattering techniques.
(12) Manning, G. *J. Chem. Phys.* **1969**, *51*, 924, 934, 3249.
(13) Soumpasis, D. *J. Chem. Phys.* **1978**, *69*, 3190.
(14) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(15) Stockmayer, W. H. *J. Polym. Sci.* **1955**, *15*, 595.
(16) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *68*, 4878.
(17) Domb, C. *Adv. Chem. Phys.* **1969**, *15*, 229.
(18) Wall, F. T.; Erpenbeck, J. J. *J. Chem. Phys.* **1959**, *30*, 634, 637.
(19) Alexandrowitz, Z.; Accad, Y. *J. Chem. Phys.* **1971**, *54*, 5338.
(20) de Gennes, P. G. *Phys. Lett. A* **1972**, *38A*, 339.
(21) le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.
(22) Smith, N. C.; Flemming, R. J. *J. Phys. A* **1975**, *8*, 938.
(23) Flemming, R. J. *J. Phys. A* **1979**, *12*, 2157.
(24) Farnoux, B.; Bouê, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Paris)* **1978**, *39*, 77.
(25) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(26) For a theoretical discussion of the threshold for asymptotic behavior see ref 22.
(27) Orofino, T. A.; Flory, P. J. *J. Phys. Chem.* **1959**, *63*, 283.
(28) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(29) Fisher, L. W.; Sochor, A. R.; Tan, J. S. *Macromolecules* **1977**, *10*, 949.
(30) Raziel, A.; Eisenberg, H. *Isr. J. Chem.* **1973**, *11*, 183.
(31) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *12*, 1785.
(32) Stejskal, J.; Beneŝ, M. J.; Kratochvil, P.; Pêska, J. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1803.
(33) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1705.
(34) The question of Θ conditions for polyelectrolytes will be discussed extensively in a future publication.
(35) Scruggs, R. L.; Ross, P. D. *Biopolymers* **1964**, *2*, 593.

Molecular Structure Effects on the Dynamic Mechanical Spectra of Polycarbonates

A. F. Yee* and S. A. Smith

Research and Development Center, General Electric Company,
Schenectady, New York 12301. *Received February 22, 1980*

ABSTRACT: The dynamic mechanical spectra of molecularly modified derivatives of poly[2,2-bis(4-hydroxyphenyl)propane carbonate] are measured. The modifications consist of substitutions for the carbonyl, the isopropylidene, and the aromatic protons with various other groups. These measurements have enabled us to deduce the nature of the secondary relaxations. The low-temperature γ relaxation is associated with the motion of the monomer unit as a whole. The intermediate β relaxation is probably due to packing defects in the glassy state. Other details of the spectra are discussed.

Introduction

The mechanical properties of solid poly[2,2-bis(4-hydroxyphenyl)propane carbonate] (BPA-PC) have been the subject of numerous investigations not only because of its well-known toughness but also because it exhibits virtually all the known mechanical behavior of all glassy polymers in different combinations of time and temperature conditions. For a comprehensive review of the various

0024-9297/81/2214-0054$01.00/0 © 1981 American Chemical Society