(6) Sosnowski, T. P.; Weber, H. P. *Appl. Phys. Lett.* **1972**, *21*, 310.
(7) Cohen, Y.; Reich, S. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 599.
(8) Greener, J.; Middleman, S. *Polym. Eng. Sci.* **1975**, *15*, 1. See also: Sullivan, T. M.; Middleman, S. *J. Non-Newtonian Fluid Mech.* **1986**, *21*, 13.
(9) Spence, J. *J. Phys. Chem.* **1939**, *43*, 865.
(10) Stein, R. S. *J. Polym. Sci.* **1957**, *24*, 383.
(11) Tsvetkov, V. N.; Andreeva, L. N. *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975.
(12) Prest, W. M., Jr. U.S. Pat. No. 4,373,065, 1983.
(13) Hahn, B. R.; Wendorff, J. H. *Polymer* **1985**, *26*, 1619.
(14) Saito, H.; Inoue, T. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 1629.
(15) Werumeus Buning, G. H.; Gijsen, R. M. R. *Polym. Prepr. (Am. Chem. Soc.)* **1988**, *29*, 211.
(16) Greener, J.; Machell, J. S. *J. Appl. Polym. Sci.*, in press.
(17) Prest, W. M.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1639.
(18) Wellinghoff, S. T.; Koenig, J. L.; Baer, E. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1913.
(19) Humme, G.; Rohr, H.; Serini, V. *Angew. Makromol. Chem.* **1977**, *58/59*, 85. See also: Casper, R.; Morbitzer, L. *Angew. Makromol. Chem.* **1977**, *58/59*, 1.
(20) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 2nd ed.; Oxford University Press: London, 1975; Chapter X.
(21) Lefebvre, D.; Jasse, B.; Monnerie, L. *Polymer* **1982**, *23*, 706.
(22) The value of Δn° for PCl (0.21) is taken as the average of values reported in two studies: (a) Biangardi, H. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 903; *Makromol. Chem.* **1982**, *183*, 1785. (b) Wu, M.-S. *J. Appl. Polym. Sci.* **1986**, *32*, 3263.
(23) Chow, T. S.; Liu, C. A.; Penwell, R. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1311.
(24) Croll, S. G. *J. Appl. Polym. Sci.* **1979**, *23*, 847.
(25) E.g.: Struik, L. C. E. *Polym. Eng. Sci.* **1979**, *19*, 223.
(26) Eaton, R. F.; Willeboondse, F. G. *J. Coat. Technol.* **1980**, *52*, 63.
(27) Holten-Andersen, J.; Hansen, C. M. *Prog. Org. Coat.* **1983**, *11*, 219.
(28) Blandin, H. P.; David, J. C.; Vergnaud, J. M.; Illien, J. P.; Malizewicz, M. *Prog. Org. Coat.* **1987**, *15*, 163.
(29) Croll, S. G. *J. Coat. Technol.* **1987**, *59*, 81.
(30) The initial film thickness in the BC technique can be estimated as half the blade height (see ref 8).
(31) Adachi, K.; Fujihara, I.; Ishida, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2155.
(32) The values of Δn° for the PS/PPO blends were estimated from linear interpolation of the values for the homopolymers (see ref 21).

Osmotic Pressure of Semidilute Solutions of Flexible, Globular, and Stiff-Chain Polyelectrolytes with Added Salt

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ABSTRACT: The renormalization group theory for the concentration dependence of the osmotic pressure of neutral polymers in semidilute solutions is applied to three structural types of polyelectrolytes: flexible chains, exemplified by sodium poly(styrene sulfonate) (NaPSS); compact globular proteins; and stiff chains including DNA, pectinate, and (carboxymethyl)cellulose. Renormalization group theory predicts that the reduced osmotic pressure, $\Pi M/CRT$, is a universal function of the reduced concentration A_2MC, where A_2 is the thermodynamic second virial coefficient and M is the molecular weight. We have used it to analyze data in the literature on aqueous salt solutions of the three polyion types. The experimental results for NaPSS over a range of salt concentrations from 0.005 to 0.5 M and molecular weight from 3.2×10^5 to 1.2×10^6 in semidilute solution fall on a universal curve independent of polymer molecular weight, polymer concentration, and salt concentration. The osmotic pressure of the semidilute polyelectrolyte solution in the presence of added salt is very similar to that of neutral polymers in good solvents. The universality of $\Pi M/CRT$ vs A_2MC is also observed for globular proteins and stiff-chain macromolecules, with each structural type having its own characteristic curve. The observed high values of the reduced osmotic pressure for spherical proteins at high reduced concentration, compared with the flexible NaPSS, are due to large contributions from third and higher virial terms. Conversely, the low values for the stiff-chain molecules are due to weak contributions from higher virials. Qualitatively, these differences reflect the different interpenetrabilities of these three types of structures.

Introduction

Polyelectrolyte solutions are complicated. To the variables characterizing neutral polymer solutions—concentration, molecular weight, and solvent quality—must be added ionic strength and polyion charge. Thus, there are additional complications arising from long-ranged polyion–polyion and polyion–small ion electrostatic interactions. Despite these complications, considerable progress can be made in understanding polyelectrolyte solutions. In our previous paper,[1] we showed that renormalization group theory developed for neutral polymers[2,3] could be applied successfully to the diffusional dynamics of polyelectrolytes. In this paper we consider the application of renormalization group theory to the osmotic pressure of solutions of flexible polyelectrolytes. In addition, we consider similar universal relations for globular and rodlike polyelectrolytes, structures of particular interest in biological systems. A similar survey has been undertaken by Burchard[4a] for neutral polymers with these shapes and by Cherayil et al.[4b] for linear, star, and ring polymers.

The osmotic pressure Π of semidilute poly(styrene sulfonate) at various salt concentrations has been measured as a function of polymer concentration C by Koene et al.[5] They found that at constant salt concentration,

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Π increases with C according to a power law with an exponent close to that predicted by scaling theory for polyelectrolyte solutions in the presence of added salt.[6-9] The lack of dependence of Π on molecular weight agrees with the scaling prediction, but the salt concentration dependence of Π is in poor agreement with scaling theory.

Renormalization group theory has been developed to describe the static properties of dilute[10,11] and semidilute[2,12,13] neutral polymer solutions. It has also been applied to the transport properties of dilute solutions.[14] It has the advantage over scaling theory that it predicts the prefactors as well as the slopes of the concentration dependence of thermodynamic and dynamic properties. Wiltzius et al.[15] studied static and dynamic properties of polystyrenes in good and marginal solvents and found that the product of molecular weight M and osmotic compressibility (the derivative of the osmotic pressure Π with respect to concentration C), $M(\partial\Pi/\partial C)_T$, is a universal function of scaled concentration, independent of solvent quality and molecular weight. Burchard[4a] and Cherayil[4b] had similar success with linear, star, and ring polystyrene and other neutral polymers.

In this report we show that renormalization group theory can be successfully applied to the concentration dependence of the osmotic pressure of semidilute polyelectrolyte solutions over a hundred-fold range of salt concentrations. The reduced osmotic pressure, $\Pi M/CRT$, of polyelectrolytes in semidilute solutions is found to be a universal function of the reduced concentration A_2MC, where A_2 is the second virial coefficient and M the molecular weight. Similar "universal" behavior is also found for spherical proteins and stiff-chain molecules in concentrated solutions, though the curves for the three types of polyions are different.

Results and Discussion

Flexible Polyelectrolytes. In dilute solutions, the osmotic pressure can be expressed in the form of a virial expansion. If truncated at the first order of concentration, the reduced osmotic pressure $\Pi M/CRT$ is given by

$$\Pi M/CRT = 1 + A_2MC \qquad (1)$$

where Π is the osmotic pressure of the polymer solutions, M the molecular weight, and C the polymer concentration in g/mL. The second virial coefficient A_2 is

$$A_2 = 4\pi^{3/2}\rho(z)N_AR_F^3/M^2 \qquad (2)$$

where $\rho(z)$ is the penetration function, which is a constant (in the range 0.21–0.26) in good solvents,[4b,16a,b] N_A is Avogadro's number, and R_F is the Flory radius of the polymer (the radius of a single chain in the good solvent limit), which varies as

$$R_F \sim M^\nu \qquad (3)$$

where ν is the excluded volume exponent, close to 3/5 in a good solvent. The critical concentration C^* stands for the concentration where the macromolecular chains starts to overlap and is defined by

$$C^* \approx M/(4/3)\pi R_F^3N_A \qquad (4)$$

From eq 1–4, we have

$$\Pi M/CRT = 1 + 1.12(C/C^*) \qquad (5)$$

where (C/C^*) is the reduced concentration showing the degree of coil overlapping.

In the scaling approach to the osmotic pressure of neutral polymer solutions in the semidilute regime, Π should obey the following relation according to des Cloizeaux[12]

$$\Pi M/CRT \approx \Omega(C/C^*) \qquad (6)$$

where Ω is a dimensionless function depending only on the ratio C/C^*. In the large overlap limit, Π should be independent of molecular weight, which implies that Ω should scale as a simple power law $(C/C^*)^m$. Combining eq 3, 4, and 6, this leads to the expression for the osmotic pressure in the semidilute solution:[12]

$$\Pi M/CRT \sim (C/C^*)^{1/(3\nu-1)} \qquad (7)$$

In the good solvent limit for neutral polymers, $1/(3\nu - 1) \approx 1.25$. This scaling prediction is in good agreement with the experimental data on semidilute poly(methylstyrene) solutions.[16a]

Odijk[7] argued that the same relations should apply to semidilute polyelectrolyte solutions in the presence of added salt, provided the influence of electrostatic interactions between the fixed charges on the macromolecular chains is taken into account. Using a Debye–Hückel type of interaction potential between the fixed charges with a screening length κ^{-1}, defined by

$$\kappa^2 = 8\pi QN_AI \qquad (8)$$

where I is the ionic strength and the Bjerrum length Q is defined by

$$Q = e^2/\epsilon kT \qquad (9)$$

e is the elementary charge, ϵ the dielectric constant of the solvent, and kT the thermal energy. Odijk[7] gave the osmotic pressure in the semidilute regime as

$$\Pi/CRT \sim A^{9/4}(L_t/\kappa)^{3/4}C^{1.25} \qquad (10)$$

where L_t represents the total persistence length of the charged macromolecules. It has been shown[7-9] that L_t may be approximated by a sum of two terms, an intrinsic part L_p and an electrostatic part L_e

$$L_t = L_p + L_e = L_p + (Q/4\kappa^2A^2f^2) \qquad (11)$$

where A is the linear charge spacing along the chains and f gives the effective charge on the polyelectrolyte chain according to counterion condensation theory.[17] For $A < Q$, $f = Q/A$, while for $A > Q$, $f = 1$.

Experimentally, for the polyelectrolyte NaPSS, ν shows a dependence on salt concentration.[20] In the salt range from 0.005 to 0.5 M NaCl and molecular weight range from 1.61×10^5 to 2.3×10^6, the average value of ν is 0.55. This gives $1/(3\nu - 1) = 1.54$ for the exponent in eq 10.

The renormalization group theoretical results for the concentration dependence of Π for neutral polymer solutions were derived in detail by Ohta and Oono et al.[2] From their final results for the renormalized osmotic pressure, we obtain the following expression for the monodisperse polymer system in the good solvent limit:

$$\Pi M/CRT = 1 + (X/2)\exp\{(\epsilon'/4)[1/X - [1/X^2 - 1]\ln(1 + X)]\} \qquad (12)$$

X is a reduced concentration, related to the second virial coefficient A_2 by

$$X[9/16 - 1/8\ln(M_w/M_n)] \approx A_2MC \qquad (13)$$

According to first-order renormalization group theory, the order of the expansion leading to eq 12 is $\epsilon' = 4 - d$, where d is the spatial dimensionality. To have agreement with the full renormalization group asymptotic result, the precise ν should be used[2] instead of 3/5 in the expres-

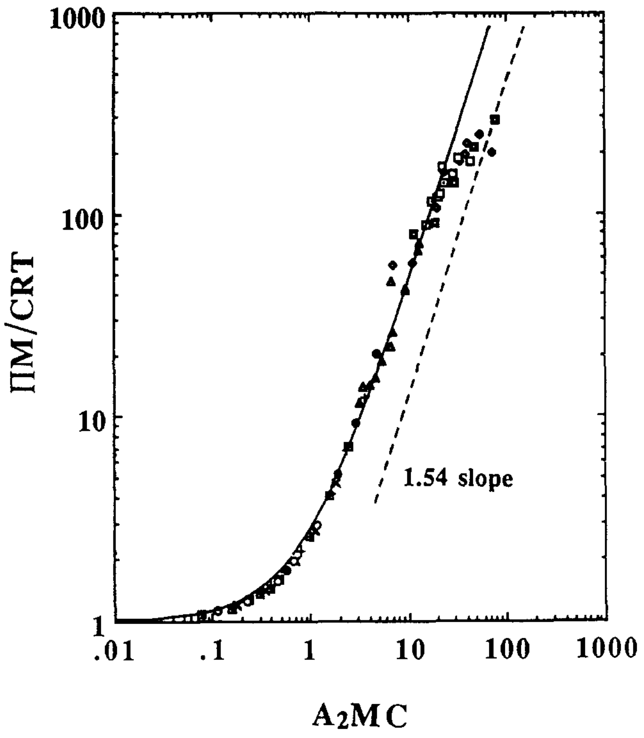

Figure 1. The normalized osmotic pressure $\Pi M/CRT$ as a function of the reduced concentration A_2MC (A_2 being the second virial coefficient) for various molecular weight NaPSS at different salt concentrations. Experimental data of osmotic pressure are taken from Koene et al.[5] and Takahashi et al.[19] and A_2 values from Takahashi et al.[19,20] Molecular weight of sodium poly(styrenesulfonate) in g/mol and NaCl concentrations are 1.2×10^6, 0.01 M (□), 4.0×10^5, 0.01 M (⊡), 6.5×10^5, 0.005 M (◇), 6.5×10^5, 0.01 M (□), 6.5×10^5, 0.05 M (△), 6.5×10^5, 0.1 M (▲), 3.2×10^5, 0.005 M (●), 3.2×10^5, 0.01 M (+), 3.2×10^5, 0.02 M (□), 3.2×10^5, 0.05 M (×), 3.2×10^5, 0.1 M (○), 3.2×10^5, 0.5 M (□). The dashed line has the slope of 1.54 predicted from scaling theory with $\nu = 0.55$, the averaged experimental value in the similar ranges of salt concentrations and molecular weights.[20] The solid curve is calculated from renormalization group theory, eq 12 and 13 for the monodispersed system,[2] $\epsilon'/4$ being replaced with $(2 - d\nu)/(d\nu - 1)$.

sion $\epsilon'/4 = (2 - d\nu)/(d\nu - 1)$. The two expressions agree when $\nu = 3/5$. The renormalized group theoretical results agree well with the experimental results for poly(α-methylstyrenes) in toluene,[16a] polystyrenes in toluene and methyl ethyl ketone,[15] and various other neutral polymer systems.[4,18]

We have applied this analysis to osmotic pressure data tabulated by Koene et al.[5] and Takahashi et al.[19] on aqueous salt solutions of NaPSS. The samples used by Koene et al.[5] were characterized by the manufacturer as having $M_w/M_n = 1.1$ and a degree of sulfonation close to unity. The sample used by Takahashi et al.[19] was temperature reduction fractionated with $M_w = 430\,000$ and $M_n = 320\,000$. The osmotic pressures were measured by membrane osmometry. The thermodynamic second virial coefficients A_2 were obtained from the tabulations of Takahashi et al.,[19,20] who determined them by elastic light scattering and osmometry. If A_2 values at certain salt concentrations were not available, they were obtained by interpolation.

A plot of log $\Pi M/CRT$ vs log A_2MC at salt concentrations from 0.005 to 0.5 M for four different molecular weights in the range 3.2×10^5 to 1.2×10^6 is shown in Figure 1. The polymer concentration varies from 0.5 to 30 g/L. This figure shows that $\Pi M/CRT$ is a function of A_2MC independent of molecular weight and salt concentration over the entire range of polymer concentration. This is particularly noteworthy since the data are from two research groups using samples from different sources.

The dashed line in Figure 1 has the slope of 1.54 predicted by scaling theory (eq 7 and 10), given the average ν value of 0.55 over this range of salt concentration. The experimental data are in reasonable agreement with this prediction. However, a scaling theory plot of log $\Pi(\kappa/L_t)^{3/4}$ vs log C does not give a single curve for all salt concentrations.[5] In contrast, using the reduced variable form in Figure 1 gives impressively universal behavior.

The solid line in Figure 1 gives the calculated values for a good solvent from the renormalization group theory eq 12 and 13, using $\epsilon'/4 = (2 - d\nu)/(d\nu - 1)$ with $\nu = 0.55$. We have not considered sample polydispersity, since its effect is very small.[2] Agreement of this theory, developed for neutral polymers, is surprisingly good for the semidilute polyelectrolyte NaPSS, since there are no adjustable parameters and no vertical rescaling of any kind. If we use $\nu = 0.6$ (approximately the good solvent limit), a discrepancy between theory and experiment for larger values of C is observed (data not shown). The underestimation by theory of $\Pi M/CRT$ at A_2MC values somewhat above 1.0 was also observed for neutral polymer solutions[2,4,15] and was ascribed to the first-order approximation used in the theory.[2,15] Furthermore, as also with polystyrene in toluene and methyl ethyl ketone, there is no solvent quality effect on Π over the entire polyelectrolyte concentration range. That is, $\Pi M/CRT$ is simply a universal function of A_2MC essentially independent of both molecular weight and solvent quality for both neutral polymer and polyelectrolyte solutions. This contrasts with the solvent quality effect to cooperative diffusion coefficients for both neutral polymers[15] and polyelectrolytes.[1]

The reduced osmotic pressure turns toward the horizontal at high values of A_2MC in Figure 1. Similar behavior has been summarized for various neutral polymer solutions by Burchard,[4] who points out that the universal behavior of flexible chains as a function of A_2MC is observed only up to a certain concentration which appears to be a characteristic of the chemical nature of the chain. Beyond this concentration the osmotic modulus shows a turnover, strong excess low angle scattering is observed, and the light scattering time autocorrelation function shows evidence of slow as well as fast diffusional motion. These anomalies are attributed to cluster formation.[4] It is quite possible that clusters are formed at high polyelectrolyte concentrations (~25–29 g/L NaPSS) and very low salt concentrations (0.005–0.01 M NaCl) corresponding to $A_2MC > 25$ in Figure 1. The molar concentration of monomer units is 10–20 times the added salt concentration in these conditions. A slow diffusion mode has been reported by many research groups[21-23] in solutions of NaPSS under similar experimental conditions. Thus we tentatively ascribe the downturn phenomenon in Figure 1 to cluster formation.

Spherical Proteins. Ree and Hoover[24] formulated the compressibility equation for rigid spherical particles and evaluated the virial coefficients B_2 to B_7 for a hard-sphere potential. The osmotic pressure of a solution of spherical polymers is

$$\Pi M/CRT = 1 + 4vC + 10(vC)^2 + 18.36(vC)^3 + 28.24(vC)^4 + 39.5(vC)^5 + 56.4(vC)^6 + \ldots \quad (14)$$

where v is the specific volume of the equivalent sphere. For a real protein, v depends on size, hydration, polyion charge, ionic strength, and other interactions in ways that

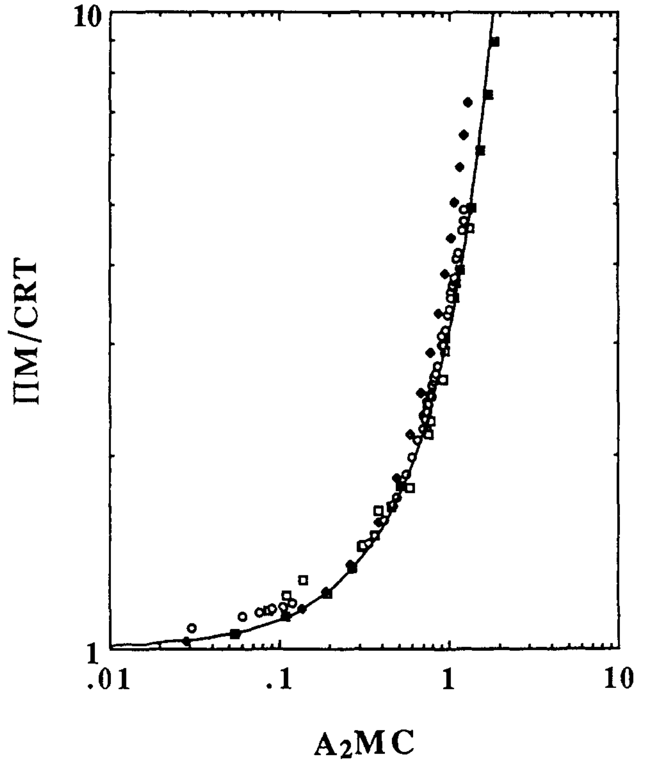

Figure 2. The normalized osmotic pressure $\Pi M/CRT$ as a function of the reduced concentration A_2MC for sheep hemoglobin (□) in 0.1 M KCl and phosphate buffer,[27] egg albumin (○), bovine serum albumin (■), and bovine methemoglobin (♦) in 1 M NaCl.[28] The solid curve is based on the calculated values from eq 14, 15, and 16.

are imperfectly understood. However, Minton[25] showed that eq 14 can be successfully applied to solutions of spherical proteins over a very broad concentration range, using υ as an empirical parameter. A numerically equivalent expression for Π, obtained from an equation of state for rigid spheres,[26] is

$$\Pi M/CRT = \{1 + \upsilon C + (\upsilon C)^2 - (\upsilon C)^3\}/\{1 - \upsilon C\}^3 \quad (15)$$

Equations 14 and 15 fit very well to Π vs C data for several proteins. These include hemoglobin in 0.1 M KCl and phosphate buffers at 0 °C[25,27] (M = 69 700, υ = 0.96 mL/g) and egg albumin in 1 M NaCl at 24 °C[28] (M = 45 000, υ = 0.748). Similar results have been obtained by light scattering for eye lens crystallin proteins.[29] Spherical proteins appear to follow the osmotic modulus curve for hard spheres very closely.

From eq 14, it is obvious that

$$A_2M = 4\upsilon \quad (16)$$

Therefore, $\Pi M/CRT$ should be a universal function of A_2MC for spherical proteins, just as it is for flexible neutral polymers and polyelectrolytes. This is demonstrated for four different proteins—sheep hemoglobin, bovine methemoglobin, bovine serum albumin, and egg albumin—in Figure 2. Data for egg albumin over the range of NaCl concentrations from 0.1 to 4.5 M[28] also fall on this curve (data not shown). The protein concentrations range as high as 400 g/L. Thus, although high quality data are limited, it appears that $\Pi M/CRT$ vs A_2MC universality may be valid for solutions of spherical proteins, independent of salt concentration, charge, or specific chemical characteristics.

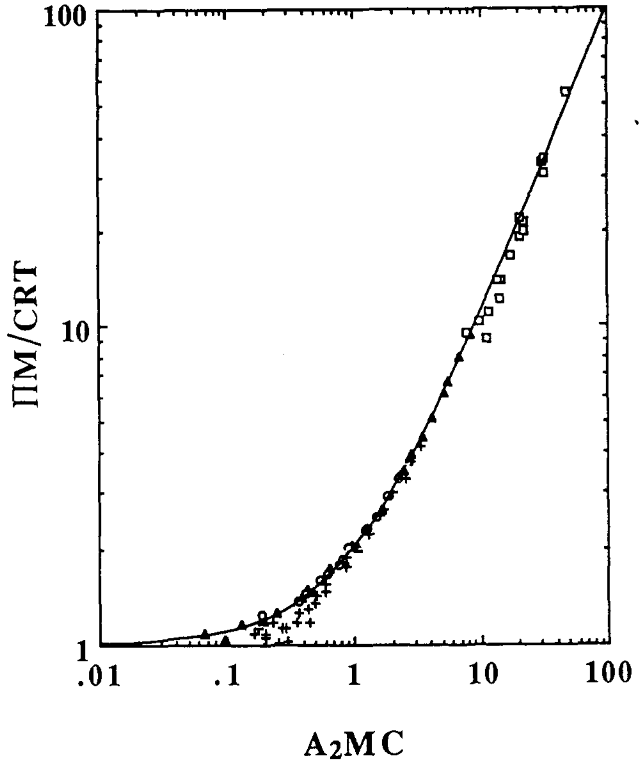

Figure 3. The normalized osmotic pressure $\Pi M/CRT$ as a function of the reduced concentration A_2MC for solutions of stiff-chain molecules: 150 bp DNA[36] (+), Col E1 plasmid DNA[37] (□), sodium pectinate[38] (▲), and sodium (carboxymethyl)cellulose[38] (○) at different salt concentrations. The solid curve is calculated from eq 1.

Rodlike and Stiff-Chain Molecules. The theory of the excluded volume for rigid rods has been solved independently by Zimm,[30] Onsager,[31] and Schulz.[32] The resulting expression for the second virial coefficient of rigid rods of length L and diameter d is[33]

$$A_2 = (\pi/4)L^2dN_AM^{-2}H \quad (17)$$

where H can be written as

$$H = 1 + (3 + \pi)(d/L)/2 + (4/\pi)(d/L)^2 \quad (18)$$

Here only hard-core interactions are taken into account. The third virial coefficient is negligible.[31,34] When all virial coefficients up to the seventh are included, the virial expansion appears to converge well for the isotropic phase.[34] The treatment has been extended to charged rodlike macromolecules in univalent salt solutions by expressing the effect of the pairwise repulsion as an increased diameter, d_B, of the charged rods.[9,35] Data on two stiff-chain polyelectrolytes—DNA[36,37] and sodium pectinate[38]—fit fairly well to these theories, when reasonable values are chosen for the effective linear charge densities and persistence lengths.

$\Pi M/CRT$ vs A_2MC for DNA, sodium pectinate, and sodium (carboxymethyl)cellulose (CMC) are plotted in Figure 3. DNA points at the low end of the curve are taken from the A_2 light scattering determinations by Nicolai and Mandel[36] on 150 base pair DNA (M = 99 000) over the range 0.002–0.5 M salt. The high end data come from osmometric measurements by Yarmola et al.[37] on Col E1 plasmid DNA (7000 base pairs, $M = 4.3 \times 10^6$) at concentrations from 1 to 4 g/L over the salt range 0.01–0.1 M. The data on sodium pectinate (M = 46 000), at polymer concentrations from 1 to 10 g/L over the range 0.003–0.5 M NaCl are from Pals and Hermans.[38] The same authors obtained the CMC data on polymers with M = 64 000 and 86 000 at concentrations from 2.6 to 7.8 g/L over the range 0.04–1.0 M salt.

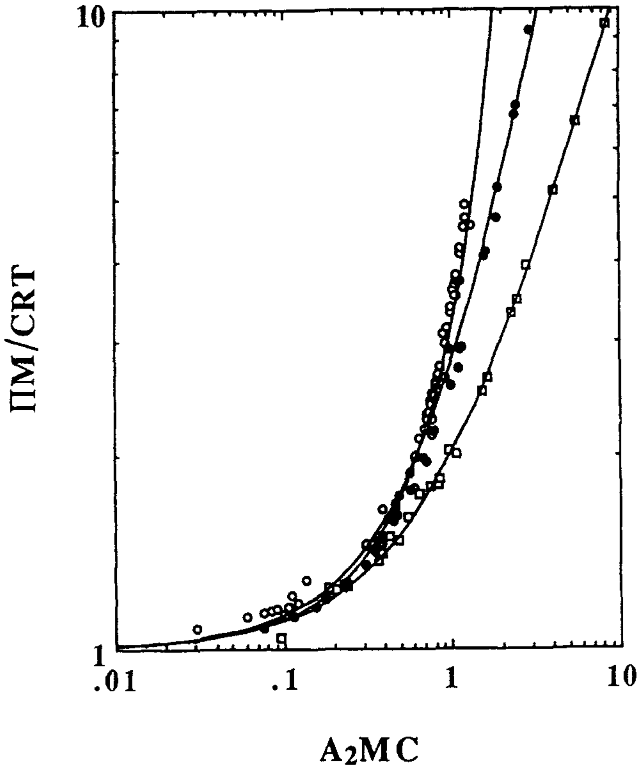

Figure 4. Comparison of osmotic pressure behavior for spherical (○), random coil (●), and stiff-chain (□) polyelectrolytes. Experimental data and theoretical curves are the same as in Figures 1, 2, and 3.

Once again, different types of polyelectrolytes, over a considerable range of molecular weight and salt concentration, fall on a universal curve. These can all be considered wormlike chains, with persistence lengths that depend somewhat on ionic strength, but are about 500 Å for DNA and 172 Å for CMC. The 150 base pair DNA can be modelled fairly well as a rigid rod, since its contour length is about one persistence length. The Col E1 plasmid must be considered as a fully developed wormlike chain, as are the pectinate and CMC. Pals and Hermans[38] observed that the reduced osmotic pressure for pectinate and CMC varied linearly with polymer concentration, consistent with a universal dependence of $\Pi M/CRT$ on A_2MC. It is striking that DNA, with quite different stiffness and charge density, falls on the same curve.

Conclusions

Our results show that the three structural types of polyelectrolytes—flexible chains, globular proteins, and rodlike or stiff chains—each exhibit a universal dependence of reduced osmotic pressure $\Pi M/CRT$ on reduced concentration A_2MC. Similar behavior was noted for neutral polymers by Burchard.[4] The curves for these three structures are plotted together in Figure 4. They differ in a way that can be understood qualitatively on the basis of the different compressibilities of the polymer forms. The curve for spherical molecules rises most steeply at high A_2MC, reflecting the excluded volume barriers to interpenetration at high volume fraction. The flexible chain curve initially resembles that for spheres but rises more gently at high reduced concentration, since the chains can interpenetrate when the average center-to-center distance becomes less than the radius of gyration. The curve for stiff chains has the lowest slope, reflecting the small contribution from third and higher virial coefficients and the ability of rods at high density to avoid overlaps by alignment.

The strong similarity between polyelectrolytes and neutral polymers indicates that the main effect of the polyion charge and its interaction with the surrounding ion atmosphere is to enlarge the polymer diameter by an amount related to the Debye screening length in the solution. With this refinement, the effects of different molecular weights, polymer concentrations, and intersegment interactions seem to be remarkably well unified by the choice of reduced variables suggested by renormalization group theory.

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Registry No. NaPSS, 9080-79-9; sodium (carboxymethyl)cellulose, 9004-32-4; sodium pectinate, 9005-59-8.

References and Notes

(1) Wang, L.; Bloomfield, V. A. *Macromolecules* **1989**, *22*, 2742.
(2) Ohta, T.; Oono, Y. *Phys. Lett.* **1982**, *89A*, 460. Oono, Y. *Adv. Chem. Phys.* **1985**, *61*, 301.
(3) Oono, Y.; Baldwin, P. R. *Phys. Rev. A* **1986**, *33*, 3391. Oono, Y.; Baldwin, P. R.; Ohta, T. *Phys. Rev. Lett.* **1984**, *53*, 2149.
(4) (a) Burchard, W. *Makromol. Chem., Macromol. Symp.* **1988**, *18*, 1. (b) Cherayil, B. J.; Bawendi, M. G.; Miyake, A.; Freed, K. F. *Macromolecules* **1986**, *19*, 2770.
(5) Koene, R. S.; Nicolai, T.; Mandel, M. *Macromolecules* **1983**, *16*, 231.
(6) de Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 1461.
(7) Odijk, T. *Macromolecules* **1979**, *12*, 688. Odijk, T. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 477.
(8) Odijk, T.; Houwaart, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
(9) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863. Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(10) de Gennes, P. G. *Phys. Lett.* **1972**, *38A*, 339.
(11) Oono, Y.; Ohta, T.; Freed, K. F. *J. Chem. Phys.* **1981**, *74*, 6458. Oono, Y.; Freed, K. F. *J. Phys. G.* **1982**, 1931. Douglas, J.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854.
(12) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 281; *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 1199.
(13) Schäfer, L. *Macromolecules* **1982**, *15*, 652; **1984**, *17*, 1357. Ohta, T.; Nakanishi, A. *J. Phys. G* **1983**, *16*, 4155. Nakanishi, A.; Ohta, T. *J. Phys. G* **1985**, *18*, 127.
(14) Oono, Y. *J. Chem. Phys.* **1983**, *79*, 4629. Oono, Y.; Kohmoto, M. *Phys. Rev. Lett.* **1982**, *49*, 1397. Jasnow, D.; Moore, M. A. *J. Phys. (Les Ulis, Fr.)* **1978**, *38*, L467.
(15) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183; **1984**, *53*, 834.
(16) (a) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 668. (b) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180. Miyaki, Y.; Einaga, Y.; Hirose, T.; Fujita, H. *Macromolecules* **1977**, *10*, 1356.
(17) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
(18) Chu, B.; Lee, D.-C. *Macromolecules* **1986**, *19*, 1592.
(19) Takahashi, A.; Kato, N.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 944.
(20) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001. Kawaguchi, M., private communication, 1984.
(21) Bloomfield, V. A. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum Press: New York, 1985; p 363.
(22) Schurr, J. M.; Schmitz, K. S. *Annu. Rew. Phys. Chem.* **1986**, *37*, 271.
(23) Drifford, M.; Dalbiez, J. P. *J. Phys., Lett.* **1985**, *46*, L-311.
(24) Ree, F. H.; Hoover, W. G. *J. Chem. Phys.* **1964**, *40*, 939; **1967**, *46*, 4181.
(25) Minton, A. P. *Mol. Cell. Biochem.* **1983**, *55*, 119.
(26) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.
(27) Adair, G. S. *Proc. R. Soc. London, Ser. A* **1928**, *120*, 573.
(28) Bull, H. B.; Breese, K. *Arch. Biochem. Biophys.* **1972**, *149*, 164; **1968**, *72*, 1817.
(29) Delaye, M.; Tardieu, A. *Nature* **1983**, *302*, 417. Delaye, M.; Gromiec, A. *Biopolymers* **1983**, *22*, 1203.
(30) Zimm, B. H. *J. Chem. Phys.* **1946**, *14*, 164.
(31) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.

Macromolecules **1990,** *23,* 199–210

(32) Schulz, G. V. *Z. Naturforsch.* **1947,** *2A,* 348.
(33) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(34) Zwanzig, R. *J. Chem. Phys.* **1963,** *39,* 1714.
(35) Stigter, D. *Biopolymers* **1977,** *16,* 1435.
(36) Nicolai, T.; Mandel, M. *Macromolecules* **1989,** *22,* 438.
(37) Yarmola, E. G.; Zarudnaya, M. I.; Lazurkin, Yu. S. *J. Biomol. Struct. Dynam.* **1985,** *2,* 981.
(38) Pals, D. T. F.; Hermans, J. J. *Recl. Trav. Chim. Pays-Bas* **1952,** *71,* 433, 458.

Cross-Polymerization of Poly(α,ω-alkyldiyne) Macromonomers

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ABSTRACT: The solid-state cross-polymerization reactions of several poly(α,ω-alkyldiyne) macromonomers $[-\mathrm{C}\equiv\mathrm{CC}\equiv\mathrm{C}(\mathrm{CH}_2)_n-]_x$ (where n = 3, 5, and 8) were characterized. UV–vis and resonance Raman spectra were recorded as a function of conversion, and the results show that a broad distribution of conjugation lengths is present in the partially cross-polymerized macromonomers. Results from samples in which the cross-polymerization was initiated with UV light were compared with those obtained by using samples that were thermally initiated. It was found that the distribution of conjugation lengths is probably caused by constraints imposed upon the growing poly(diacetylene) (PDA) chains by the crystallite size distribution and the crystallite defect density distribution of the sample as well as by UV-induced chain degradation (for those samples that were initiated with UV light). Resonance Raman spectra of the three macromonomer systems investigated show that the low-frequency bands are mixed modes that are primarily due to motions of the aliphatic spacer groups. The intensity behavior of the 720 and 1211 cm^{-1} bands indicates that a structural change takes place in the aliphatic side chains after about 1 min of UV exposure.

1. Introduction

Perhaps the most basic characterization parameter for a diacetylene material is the extent of conversion of the diacetylene reaction. The degree of conversion affects virtually all physical properties of the material. This parameter may be even more significant for the class of materials referred to as diacetylene macromonomers than for conventional diacetylenes, since the diacetylene polymerization in the macromonomers results in cross-linking within the crystalline regions.[1,2] Although this "cross-polymerization" reaction differs from conventional polymer cross-linking processes, one would expect many of the same types of physical property modifications to result from cross-polymerization as from more conventional cross-linking. For this reason, it is important to have a full understanding of how the structure of the macromonomer changes as a function of the degree of conversion. The work presented here is specifically concerned with understanding the structural changes which take place upon cross-polymerization of the poly(α,ω-alkyldiyne)'s, whose general structure is

$$[-\mathrm{C}\equiv\mathrm{CC}\equiv\mathrm{C}(\mathrm{CH}_2)_n-]_x$$

Although the degree of conversion is a very basic quantity, it is difficult to measure quantitatively for the macromonomers. The most common technique used to determine the degree of conversion in conventional diacetylene systems is the monomer extraction method. In principle, monomer extraction is a very simple technique. A diacetylene monomer sample of known weight is exposed to high-energy radiation (or thermal annealing) for a given amount of time. The sample is then immersed in a solvent that will dissolve the monomer but leave the polymeric portion of the sample intact. The insoluble portion of the sample is recovered, thoroughly dried, and then weighed. The degree of conversion is determined by the ratio of the weight of recovered insoluble material to the weight of the original sample.

Despite the conceptual simplicity of the monomer extraction method, there are some complicating factors, even in the case of conventional diacetylene systems. At low conversions, the small amount of insoluble material formed may be difficult to fully recover, leading to an underestimation of the degree of conversion. At high conversions it is possible that small "pockets" of unreacted monomer could be trapped within a matrix of insoluble polymer. This effect would lead to an overestimation of the degree of conversion.[3]

The extraction method has even more severe drawbacks when applied to the macromonomers. If any portion of a particular macromonomer chain is incorporated into a cross-polymerized region of the sample, the whole chain will be rendered insoluble, leading to a gross overestimation of the degree of conversion. Clearly then, the monomer extraction technique is not a suitable method for determining the extent of cross-polymerization in the macromonomer systems (although we will see later that other useful information about the macromonomers can be gained from this technique).

Another method that can be used to determine the degree of reaction in conventional diacetylene systems is UV spectroscopy.[4] There is a weak monomer absorption (with associated vibronic peaks) at about 250 nm due to the diacetylene unit. As the polymerization pro-

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