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Conformational Properties of Bolaform Electrolytes

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ABSTRACT: Average configuration-dependent physical properties have been evaluated for polymethylene chains bearing similarly charged ends. The polymethylene chain contains upward from 20 bonds, and the dielectric constant of the medium ranges upward from 3.5. Configuration-dependent properties evaluated were the persistence vector, average center-of-mass vector, mean-square end-to-end distance, mean-square radius of gyration, averages of corresponding moments of the inertia tensor, and the probability of observation of a trans placement at an internal bond in the chain. The perturbation produced by the charged ends disappears at sufficiently large chain length. However, a large number of bonds (well in excess of 300) may be required to eliminate the effect of the perturbation. The characteristic ratio goes through a maximum at finite chain contour length in media of low dielectric constant. This behavior is not restricted to bolaform electrolytes formed from polymethylene. It will be observed with any flexible bolaform electrolyte. Significant expansion of the chain, and alteration in the asymmetry of the distribution of chain atoms, can be observed even when the probability for a trans placement is indistinguishable from that found in the unperturbed chain. While the alteration in the distribution of chain atoms serves to increase the asymmetry, the perturbed molecules are still more accurately described as random coils than as rods with charged ends.

Possibly the simplest class of molecules that possess some polyion characteristics are the bolaform electrolytes, i.e., molecules of chemical structure $Y^-X^+(CH_2)_xX^+Y^-$.[1] Primary (K_1) and secondary (K_2) dissociation constants for bolaform electrolytes would differ by a factor of 4 if there were no interaction of the identical groups at opposite ends of the polymethylene chain. Electrostatic interaction of the end groups causes K_1/K_2 to actually be greater than 4. In addition to modifying the dissociation constants, the electrostatic stress present in the completely dissociated bolaform electrolyte, X^+–$(CH_2)_x$–X^+, perturbs configuration-dependent properties of the intervening polymethylene chain. The repulsion between charged ends is minimized when the end-to-end distance is at its upper limit, i.e., when the polymethylene chain is in the planar zigzag configuration with all bonds occupying trans states. This configuration could be modeled as a rod with charged ends. The tendency for the bolaform electrolyte to become rodlike is opposed by the tremendous reduction in configurational entropy associated with complete suppression of configurations containing one or more gauche placements. In general, one expects the balance between these two effects to produce configuration-dependent properties lying somewhere between those associated with the unperturbed and fully extended chains.

Our objective here is to characterize configuration-dependent properties of bolaform electrolytes in which the only perturbation of the polymethylene chain is that arising from the electrostatic interaction of similarly charged ends. Of particular interest are the magnitudes of the chain expansion, alteration in the probability for observation of a trans placement, and distortion of the average asymmetry of individual chain configurations (including an assessment of the appropriateness of a model in which the bolaform electrolyte is taken to be a rod with charged ends).

Calculations

Representative Samples of Chains. Representative samples of unperturbed polymethylene chains containing n bonds were generated by using a rotational isomeric state model which successfully rationalizes configuration-dependent properties of unperturbed polymethylene.[2,3] In this model the C–C bond length, l, and CCC angle are held constant at 153 pm and 112°, respectively. Three rotational states, with dihedral angles of 0° and ±120°, are accessible to each internal bond. Weighting of these rotational states assumes isolated gauche states are 500 cal mol^{-1} higher in energy than trans states, and successive gauche placements of opposite sign elevate the energy an additional 2000 cal mol^{-1}. The temperature is taken to be 140 °C.

If the small[4] end effects in unperturbed polymethylene are ignored, representative chains can be generated by using the above geometry and the following set of conditional probabilities:

$$\mathbf{Q}_{\xi\eta} = \begin{bmatrix} 0.5396 & 0.2302 & 0.2302 \\ 0.6830 & 0.2914 & 0.0256 \\ 0.6830 & 0.0256 & 0.2914 \end{bmatrix} \qquad (1)$$

Here each element, $q_{\xi\eta}$, is the conditional probability that a bond will be in rotational state η, given that its predecessor occupies rotational state ξ. Rows index the state of the preceding bond, columns index the state of the bond in question, and the order of indexing is trans (t), gauche$^+$ (g$^+$), gauche$^-$ (g$^-$). This expression was used for bonds 3 to $n - 1$, and the first row was used for bond 2.

Each chain is weighted according to $\exp(-e^2/DrkT)$, where e, D, r, k, and T denote, respectively, the electronic charge, dielectric constant, end-to-end distance, Boltzmann's constant, and absolute temperature. Calculations were performed by using 3.5, 10, 35, 100 and ∞ for the dielectric constant. Using $D = \infty$ simply yields the unperturbed chain, while $D = 3.5$ is approximately correct for many organic solvents. Neither counterions nor a supporting electrolyte is taken into consideration in the weighting scheme. If counterions or a supporting electrolyte were present, they would serve to cause all weighting factors to lie closer to unity, thereby diminishing the perturbation produced by the similarly charged ends.

Chains with n lying between 20 and 300 were studied. At each n, 50×10^3 chains were generated and divided into five sets of 10×10^3 chains each. Configuration-dependent properties were averaged for the weighted chains in each group. Error bars for plotted points denote ±1 standard deviation, assessed from the averages for the five sets of 10×10^3 chains each.

Configuration-Dependent Properties. The persistence vector, $\mathbf{a}$, is the average of the vector from the zeroth to the nth chain atom. This vector, as well as others presented below, is expressed in a local coordinate system established by the first two bonds in the chain. The coordinate system originates at the zeroth atom. The X axis lies along the first bond, and the Y axis is in the plane of

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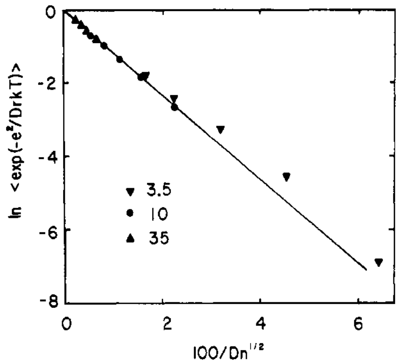

Figure 1. Severity of the electrostatic interaction, measured by ln $\langle \exp(-e^2/DrkT) \rangle$, as a function of $1/Dn^{1/2}$ for D = 3.5, 10, and 35.

the first two bonds. Directions for these axes are chosen so that the x and y components for the first three atoms are nonnegative.

The center-of-mass vector for a specified configuration is

$$\mathbf{g} = (n + 1)^{-1}\sum_{i=0}^{n}\mathbf{r}_{0i} \qquad (2)$$

where $\mathbf{r}_{0i}$ denotes the vector from the zeroth to the ith chain atom. The average center-of-mass vector is denoted by $\langle \mathbf{g} \rangle$.

Each configuration has an inertia tensor given by

$$\mathbf{S}_{x2} = (n + 1)^{-1}\sum_{i=0}^{n}\mathbf{r}_{0i}^{x2} - \mathbf{g}^{x2} \qquad (3)$$

where $x2$ as a superscript denotes the self-direct product and $\mathbf{S}_{x2}$ is generated as a column with the nine elements in reading order. Diagonalization of the 3 × 3 representation of $\mathbf{S}_{x2}$ yields the principal moments, $L_1^2 \geq L_2^2 \geq L_3^2$, their sum being s^2, the squared radius of gyration. Averages over all configurations are denoted by $\langle s^2 \rangle$ and $\langle L_i^2 \rangle$.

Results and Discussion

Severity of the Electrostatic Interactions. Electrostatic interaction of the similarly charged end groups causes $\exp(-e^2/DrkT)$ for each configuration to be less than unity. A measure of the strength of the electrostatic interaction is provided by the average value, $\langle \exp(-e^2/DrkT) \rangle$. If all chains generated in each sample were to have the same r, and if this r were proportional to $n^{1/2}$, ln $[\exp(-e^2/DrkT)]$ would be inversely proportional to $Dn^{1/2}$. Figure 1 depicts the behavior of ln $\langle \exp(-e^2/DrkT) \rangle$ for the sets of representative chains generated. Even though r varies from chain to chain within a sample and the chains generated are not long enough to yield $\langle r^2 \rangle_0$ proportional to n, data presented for D = 10 and 35 describe a single straight line. Data obtained with D = 3.5 fall somewhat above this line when n is 160 or smaller but nearly merge with the line when n is 300. At n = 300, $\langle \exp(-e^2/DrkT) \rangle$ is 0.49 for D = 10 but only 0.16 for D = 3.5. According to this measure, significant electrostatic interaction may persist even when several hundred methylene units connect the charged end groups.

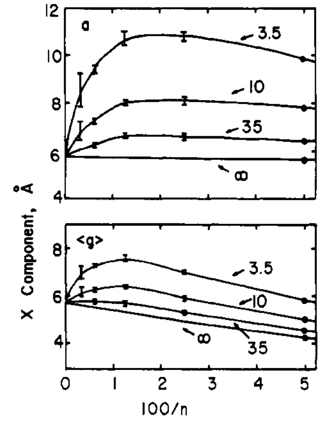

Figure 2. Behavior of the x component of **a** and $\langle \mathbf{g} \rangle$ for the indicated values of the dielectric constant. Filled circles have a radius greater than one standard deviation.

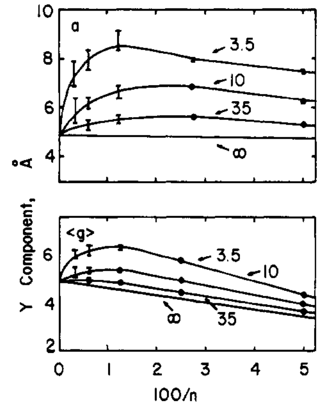

Figure 3. Behavior of the y component of **a** and $\langle \mathbf{g} \rangle$ for the indicated values of the dielectric constant. Filled circles have a radius greater than one standard deviation.

Persistence and Average Center-of-Mass Vectors. The z component is zero for the persistence and averaged center-of-mass vectors because polymethylene has a symmetric rotation potential. Figure 2 depicts the x component of these vectors, and the y component is shown in Figure 3. In the absence of any electrostatic interaction of the chain ends, both x components approach an asymptotic limit of 5.75 Å, while the y components approach 4.86 Å.[5] The persistence vector attains its limiting value at smaller n than does the average center-of-mass vector. Neither component goes through a maximum when the chain is unperturbed.

The perturbation produced by electrostatic repulsion of the chain ends increases the x and y components of both vectors for chains of finite n. As n goes to infinity, however, each vector approaches the limiting value obtained with the unperturbed chain. At infinite n only a vanishingly small fraction of the chain configurations have r small enough to produce a value for $\exp(-e^2/DrkT)$ which differs significantly from unity. Thus the infinitely long chain is unperturbed.

Extremely short chains may have small $\exp(-e^2/DrkT)$ in most (perhaps all) of the available chain configurations. The opportunity for chain expansion is limited, however, because short chains have only a small number of allowed configurations. Thus alteration in configuration-dependent properties is small at both extremes of n. In one case there are a large number of configurations, but the perturbation vanishes. In the other case an enormous interaction energy may be responsible for the perturbation, but the opportunity for alteration of configuration-dependent properties is limited by the small number of chain configurations.

The perturbation produced by the charged ends exerts its greatest effect on the persistence and average center-of-mass vectors when n is on the order of 10^2 if the dielectric constant is 3.5–10. At this n the chain has a large number (3^{n-2}) of configurations with a wide range of end-to-end and center-of-mass vectors, and there is a pro-

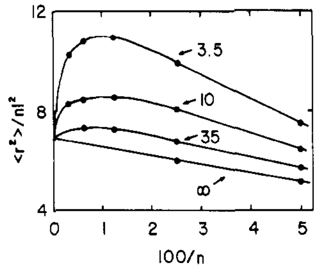

Figure 4. Characteristic ratio for bolaform electrolytes in media of the indicated dielectric constant.

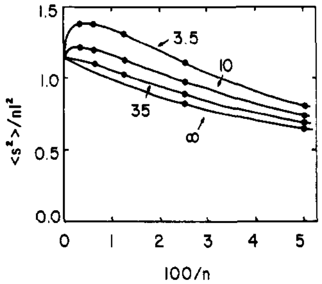

Figure 5. Mean-square radius of gyration for bolaform electrolytes in media of the indicated dielectric constant.

nounced variation in $\exp(-e^2/DrkT)$ from one configuration to the next. When the dielectric constant is 3.5, x and y components of the persistence vector can be increased by as much as a factor of 1.8–1.9. In contrast, components of the average center-of-mass vector increase by no more than a factor of 1.4. It is hardly surprising that the persistence vector is more strongly affected, because it is the length of the end-to-end vector which dictates weighting of the chains generated.

Mean-Square Dimensions. A. Monte Carlo Results. Figure 4 depicts characteristic ratios, $\langle r^2 \rangle / nl^2$, for the bolaform electrolytes. The characteristic ratio for the unperturbed chain increases with increasing n, reaching an asymptotic limit of 6.87.[6] This same asymptotic limit is attained for the chain perturbed by electrostatic interaction of its ends because the perturbation becomes insignificant as n goes to infinity. The characteristic ratio for perturbed chains, however, can go through a maximum if the dielectric constant is not too large. When the dielectric constant is 3.5, the maximum occurs when n is 10^2. The maximum expansion produced in a medium of this dielectric constant corresponds to $\alpha_r = 1.30$, where $\alpha_r^2 = \langle r^2 \rangle / \langle r^2 \rangle_0$.

The mean-square radius of gyration is much less sensitive to the perturbation, as is shown by a comparison of Figures 4 and 5. When the dielectric constant is 3.5, the largest α_s is 1.16 ($\alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$). Nonidentity of α_s and α_r implies the perturbation modifies the asymmetry of the distribution of chain atoms.

B. Relationship to Gaussian Molecules. We now examine the relationship between α_r^2 calculated in the rotational isomeric state approximation for a polymethylene chain with charged ends and α_r^2 for a Gaussian coil with identical charges on both ends. For a Gaussian molecule experiencing a perturbation in dimensions due to end-charge repulsion, it is easily demonstrated that

$$\alpha_{r,\mathrm{G}}^2 = (2/3) \int_0^\infty \mathrm{d}r\, r^4 \exp(-r^2 - b/r) \Big/ \int_0^\infty \mathrm{d}r\, r^2 \exp(-r^2 - b/r) \tag{4}$$

with $b = (e^2/DkT)(3/2\langle r^2 \rangle_0)^{1/2}$. At 140 °C, b is $50490 D^{-1} \langle r^2 \rangle_0^{-1/2}$, with $\langle r^2 \rangle_0^{1/2}$ expressed in picometers.

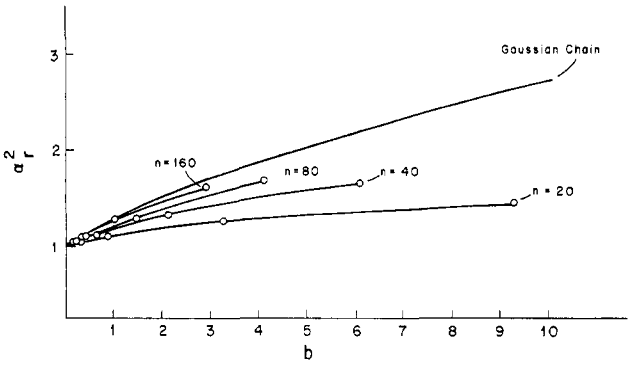

Figure 6. Expansion factor α_r^2 as a function of b for Gaussian chains and n = 20-, 40-, 80-, and 160-bond polymethylene chains.

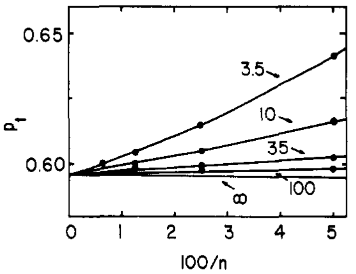

Figure 7. Probability of a trans placement for an internal bond in a bolaform electrolyte immersed in a medium of the indicated dielectric constant.

Physically b is the ratio of the characteristic length of electrostatic interactions, $l_e = e^2/DkT$, to an average distance of end-to-end separation in the unperturbed chains, $(2\langle r_0^2 \rangle/3)^{1/2}$. Large values of b indicate that l_e is greater than the mean separation of ends in the unperturbed chain; thus $\alpha_{r,\mathrm{G}}^2$ is expected to increase appreciably from unity. Numerical evaluation of eq 4 for values of b up to 95 indicates that $\alpha_{r,\mathrm{G}}^2$ is, as expected, a monotonically increasing function of b.

Figure 6 depicts α_r^2 for the Gaussian chain and for perturbed polymethylene chains where n is 20, 40, 80, and 160. Polymethylene chains with 300 bonds yield a result indistinguishable from the Gaussian limit. Note that for a given value of n, all values of α_r^2 lie on the same curve and that the family of curves converges to the Gaussian limit as n becomes large. These results can be rationalized as follows: Consider the limiting case of a two-bond chain. (In this situation, the Gaussian distribution of end-to-end distances is incorrect.[1]) The constraint of fixed bond lengths and bond angles requires $\alpha_r^2 = 1$, independent of b. However, a *Gaussian* molecule having the same $\langle r_0^2 \rangle$ can undergo chain expansion, i.e., $\alpha_{r,\mathrm{G}}^2 > 1$. In general, for a given value of n, the number of accessible configurations available to a molecule experiencing rigid bond length, bond angle, and discrete torsional minima is smaller than that of a Gaussian molecule. Consequently, we would expect the Gaussian coil to undergo a proportionately larger expansion for a given value of b than a polymethylene chain, i.e., $\alpha_{r,\mathrm{G}}^2 \geq \alpha_r^2$. In the limit of large n, the polymethylene chain approaches the Gaussian limit and thus $\lim_{n\to\infty} \alpha_r^2 = \alpha_{r,\mathrm{G}}^2$ at a fixed b, as is observed.

Probability of a Trans Placement. Figure 7 depicts the probability of a trans placement at internal bonds. In the unperturbed state, this probability approaches 0.596 at large n.[4] A significantly higher fraction of the internal bonds in the perturbed chain occupies trans placements if the dielectric constant and number of bonds are small. However, as n goes to infinity, the fraction of bonds in trans placements still approaches 0.596. Comparison of

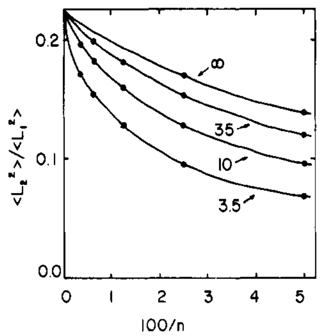

Figure 8. Ratio of $\langle L_2^2\rangle$ to $\langle L_1^2\rangle$ for bolaform electrolytes in media of the indicated dielectric constant.

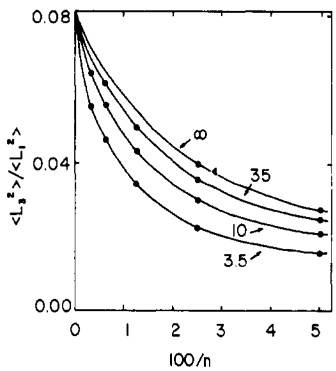

Figure 9. Ratio of $\langle L_3^2\rangle$ to $\langle L_1^2\rangle$ for bolaform electrolytes in media of the indicated dielectric constant.

Figures 4, 5, and 7 demonstrates that significant chain expansion can occur with little alteration in p_t. For example, when n is 300 and the dielectric constant is 3.5, α_r and α_s are 1.23 and 1.13, respectively, but p_t is indistinguishable from 0.596.

Bolaform electrolytes resemble a chain with one end attached to an impenetrable interface in that appreciable chain expansion can be achieved without alteration of the probability for observation of a trans placement.[7] There is, however, an important difference in the behavior of these chains. While α_r and α_s approach unity as n goes to infinity for bolaform electrolytes, the asymptotic limit for the chain with one end attached to an impenetrable interface is $\alpha_{r,\infty} > \alpha_{s,\infty} > 1$.[7,8] The intramolecular excluded-volume effect can also produce significant expansion without alteration in the probability for a trans placement.[9,10] In this case, however, neither α_r nor α_s approaches an asymptotic limit as n becomes infinite.[11]

Asymmetry of Individual Configurations. Departures from unity of $\langle L_2^2\rangle/\langle L_1^2\rangle$ and $\langle L_3^2\rangle/\langle L_1^2\rangle$ reflect the average asymmetry of the distribution of chain atoms in individual configurations. Flexible linear-chain molecules of sufficiently large n have $\langle L_2^2\rangle/\langle L_1^2\rangle = 0.225$ and $\langle L_3^2\rangle/\langle L_1^2\rangle = 0.082$.[5,12-18] At finite n, these ratios depart from their asymptotic limits in a manner specified by the local chain structure.[17] Figures 8 and 9 show that finite unperturbed polymethylene chains are more asymmetric (have smaller $\langle L_2^2\rangle/\langle L_1^2\rangle$ and $\langle L_3^2\rangle/\langle L_1^2\rangle$) than infinitely long chains, due in part to the valence angle being greater than 100°.[17] The ratio of $\langle L_3^2\rangle$ to $\langle L_1^2\rangle$ approaches its asymptotic limit more slowly than does $\langle L_2^2\rangle/\langle L_1^2\rangle$.

The perturbation produced by electrostatic interaction of the chain ends depresses $\langle L_2^2\rangle/\langle L_1^2\rangle$ and $\langle L_3^2\rangle/\langle L_1^2\rangle$ at finite n. Comparison of Figures 7–9 shows significant alteration in asymmetry may persist even when the chain is long enough so that there has been no effect on the probability for a trans placement. Examination of the individual $\langle L_i^2\rangle$ at finite n reveals that they respond differently to the perturbation. At all n in the range examined (20–300), the perturbation produces an increase in $\langle L_1^2\rangle$. Behavior of the remaining two averaged principal moments, however, depends on where n is in the range covered.

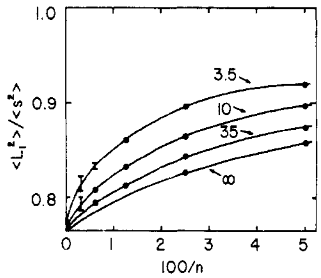

Figure 10. Ratio of $\langle L_1^2\rangle$ to $\langle s^2\rangle$ for bolaform electrolytes in media of the indicated dielectric constant.

If n is less than about 160, $\langle L_2^2\rangle$ and $\langle L_3^2\rangle$ both *decrease* when the perturbation occurs. Therefore for n in this range, individual configurations experience an expansion of the distribution of chain atoms along the major principal axis and a contraction of the distribution perpendicular to that axis. The expansion along the major principal axis outweights the contraction perpendicular to it, causing an increase in $\langle s^2\rangle$ (Figure 5). Electrostatic interaction of the chain ends perturbs the distribution of chain atoms so that its asymmetry more closely approximates that of a rod if n is less than about 160.

In contrast, the perturbation has very little effect on $\langle L_2^2\rangle$ or $\langle L_3^2\rangle$ if n is greater than about 160. The perturbation produced by the electrostatic interaction in chains with n lying between 160 and infinity simply expands the distribution of chain atoms along the major principal axis.

Rodlike Character. Since the perturbation produces an increase in $\langle L_1^2\rangle$ and either a decrease or little change in the sum of $\langle L_2^2\rangle$ and $\langle L_3^2\rangle$, it becomes worthwhile to inquire whether the changes in asymmetry are sufficient to justify describing the bolaform electrolytes as rods. If the chains with 20 or more bonds were to be fully extended in the all-trans configuration, an excellent approximation would be $\langle s^2\rangle = \langle L_1^2\rangle$, $\langle L_2^2\rangle = \langle L_3^2\rangle = 0$. For such chains $\langle L_1^2\rangle/\langle s^2\rangle$ is unity, while for flexible chains this ratio approaches 0.765 as n increases.[5,12-18]

Figure 10 depicts $\langle L_1^2\rangle/\langle s^2\rangle$ for the chains considered here. The perturbation produces an increase in this ratio at finite n. However, for all circumstances investigated, $\langle L_1^2\rangle/\langle s^2\rangle$ lies closer to the value obtained at that n for the unperturbed chain than it does to unity. On this basis the bolaform electrolytes are more accurately described as random coils than as rods.

Dielectric Effects on the Qualitative Results. Suppose the bolaform electrolyte were modeled as a low-dielectric sausage immersed in a higher dielectric constant solvent. The charges may be imagined to lie near the ends of the sausage. On the basis of previous results for spheres,[19,20] ellipsoids of revolution,[21] and cylinders,[22] when the two charges are spatially close together, we might expect up to a factor of 2 or so *increase* in the electrostatic potential, ψ, over that predicted from Coulomb's law, ψ_C. On the other hand, if the sausage is fully extended, ψ_C should be greater than ψ. In the range of n studied here, the probability of the ends being close to each other is fairly small; thus increases in ψ due to dielectric discontinuities are probably of little importance in determining configurational properties. Moreover, for organic solvents, the conformational properties of bolaforms are most likely bounded from above and below by those calculated in the range of dielectric constants (3.5-35) used here. Since the calculated quantities show the same qualitative trends throughout this range of dielectric constants, we would expect our conclusions to hold when a more sophisticated electrostatic potential is employed.

Added in Proof: If bolaform electrolytes were studied at a temperature different from the Θ temperature for polymethylene, an additional perturbation would arise from the excluded-volume effect. Since the interaction of the charged chain ends becomes negligible as n becomes infinite, the expansion arising from the excluded-volume effect would dominate for large bolaform electrolytes.

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Equation-of-State Theory Applied to Mixtures of Isotactic Poly(ethyl methacrylate) and Poly(vinylidene fluoride)

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ABSTRACT: Flory's equation-of-state theory is applied to a PVF_2/it-PEMA system with a lower critical solution temperature. A comparison is made between the observed irregular asymmetric cloud point curve and the calculated spinodals. The agreement is good for values of the mixing parameters, which are in accordance with melting point depression data.

Introduction

Over the years it has become clear that nearly all blends of miscible polymers show lower critical solution temperature (LCST) behavior. To study this, one needs polymer pairs with cloud point curves in a temperature range accessible to measurements. In this respect, the various poly(vinylidene fluoride) (PVF_2)/poly(alkyl methacrylate) systems obviously offer good prospects. In addition to the fact that many of these systems are miscible, one has the disposal of at least three parameters which affect this miscibility: the ester group, the tacticity, and the molar mass.[1-6] By a suitable adaptation of these parameters, blends with the desired properties can be obtained. A nice example, considered in this paper, is PVF_2 with low molar mass isotactic poly(ethyl methacrylate) (it-PEMA).

It is well-known that thermodynamic miscibility is only possible if the Gibbs free energy of mixing, ΔG_m, is negative, but even in that case the stability is determined by the curvature of ΔG_m as a function of composition. A strictly binary system is stable if $(\partial^2\Delta G_m/\partial\varphi_2^2)_{P,T}$ is positive over the entire composition range. So, $\Delta G_m < 0$ is a necessary but insufficient condition for polymer-polymer miscibility. A ripple in the $\Delta G_m(\varphi_2)$ curve makes a one-phase system unstable with respect to a two-phase system and partial miscibility is the result. In that case, the points of common tangency to the $\Delta G_m(\varphi_2)$ curve define the compositions of the coexisting phases (binodal) in a temperature-composition plot.

In addition there are two inflection points in the $\Delta G_m(\varphi_2)$ curve, where in between the curvature $(\partial^2\Delta G_m/\partial\varphi_2^2)_{P,T}$ is negative and the system is unstable. The limit of stability, also called the spinodal, is given by

$$(\partial^2\Delta G_m/\partial\varphi_2^2)_{P,T} = 0 \qquad (1)$$

In between the spinodal and the binodal $(\partial^2\Delta G_m/\partial\varphi_2^2)_{P,T}$ is positive, but the system is metastable because the mixture is stable toward small composition changes but unstable toward sufficiently large fluctuations. Usually, a cloud point curve (CPC) is measured, which lies in between the binodal and the spinodal. If the ripple in the $\Delta G_m(\varphi_2)$ curve disappears at decreasing temperature, an LCST will be the outcome.

Several theories have been developed to explain the LCST behavior in polymer systems. The best known examples are Flory's equation-of-state theory and the lattice fluid theory.[7,8] All these approaches adopt the classical Flory-Huggins expression for the combinatorial entropy of mixing. As a result of this contribution to the Gibbs free energy of mixing, the calculated binodals and spinodals are shifted toward the region of compositions poor in the constituent with the larger average chain length.

A cloud point curve which is characteristic for blends of low molar mass it-PEMA and PVF_2 is shown in Figure 1. The miscibility gap for these blends is located in the PVF_2-rich region of the phase diagram; the PVF_2 molecules, however, have the larger average chain length (cf.

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