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Chain Conformations of Polycarbonate from ab Initio Calculations

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ABSTRACT: Ab initio calculations with full geometry optimization on diphenyl carbonate (DPC) and diphenylpropane (DPP) are carried out to determine the bond geometries and the conformational energies and then to compute the unperturbed chain dimensions of the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane, or bisphenol A polycarbonate. The bond geometries calculated with the 6-31G* basis sets are in excellent agreement with the experimental values. The conformational energy contours exhibit a rather low energy barrier (ca. 1.9 kcal/mol) in DPP and a nearly flat profile in DPC for the rotations of phenylene groups. Moreover, the trans conformation of the carbonate group is favored by ca. 2.75 kcal/mol over the cis state. Application of these results to the rotational isomeric state model of the polycarbonate chain leads to the prediction of the unperturbed chain dimension of $\langle r^2\rangle_0/M \simeq 1.1$, which supports the previous calculation of Yoon and Flory. This calculated value is in satisfactory agreement with the experimental results of 1.2–1.3, obtained from small-angle neutron scattering from amorphous polycarbonate by Gawrisch et al. and Ballard et al.

Introduction

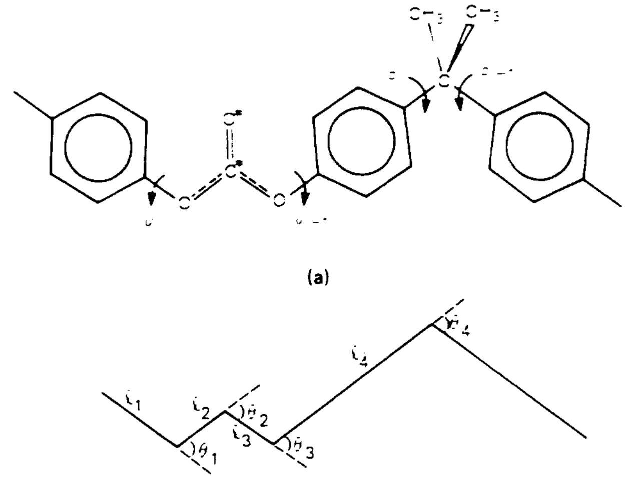
The chain conformations of the polycarbonate (PC) of 2,2-bis(4-hydroxyphenyl)propane, or bisphenol A polycarbonate, shown schematically in Figure 1a, have been studied by many authors since the first work on this topic was published by Williams and Flory in 1968.[1] The pertinent data are the conformational energies associated with the two torsional angles ϕ_i and ϕ_{i+1} within 2,2-diphenylpropane, the torsional angles ψ_i and ψ_{i+1} within diphenyl carbonate, respectively, and the energy difference between the trans and cis conformations of the carbonate group. Previous works include a number of empirical calculations,[2-6] MNDO-type semiempirical calculations,[7] and STO-3G level ab initio computations with fixed geometry.[8] The calculated conformational energies in conjunction with the geometric parameters determined separately by X-ray structure analyses of the model compounds, for example, were then applied to deduce a number of equilibrium properties.[1,4,9] Some attempts were also made to relate the conformational energetics to the unusual dynamic and mechanical properties of this polymer.[8]

Ab initio quantum mechanical calculations are widely used for the determination of equilibrium geometries, torsional barriers, and electronic excitation energies of small molecules. Recently, improvements in computer hardware and algorithms have permitted the application of these techniques to larger molecules including oligomeric models of polymers with reasonable confidence.[10,11] Ab initio calculations, therefore, have the potential of providing reliable information on bond geometries and conformational energies, when the conventional methodology is not readily applicable due to the difficulty of obtaining X-ray structural data and/or the complicated geometry–conformational energy relationships.

In this paper, we apply ab initio quantum mechanical calculations that allow full geometry optimization to the PC chain to calculate both the geometric parameters and the conformational energies involved. Different levels of basis sets are employed to determine the degree of complexity that is required to match the available experimental results of bond geometries. The bond geometries and conformational energies that are estimated employing the necessary basis sets are then used to compute the unperturbed chain dimensions of PC by the rotational isomeric state method.[1] The usefulness and the potential of the ab initio method is then tested by comparing its predicted value of the unperturbed chain dimension with available experimental results for the PC chain in dilute solutions and in the bulk amorphous state.

Computational Method

The calculations reported herein utilize standard aspects of ab initio quantum chemistry codes. For most closed-shell molecules, molecular geometries can be determined by the solution of the electronic Schroedinger equation at the Hartree–Fock or self-consistent field (SCF) level. The molecular wave function is expanded in a basis of Gaussian functions which represent



(a)

(b)

Figure 1. (a) Schematic diagram of the PC chain. (b) The schematics of the PC chain denoting symbols for the bond geometries.

atomic orbitals, and each electron experiences only the average field of the remaining electrons in the molecule.

An SCF level calculation, therefore, gives an approximate picture of the electron density distribution in a molecule. A more accurate description is obtained by allowing each electron to feel the instantaneous influence of all the other electrons in the molecule. Two examples of this scheme are the multiconfigurational self-consistent field (MCSCF) and configuration interaction (CI) methods. However, experience has shown that SCF level calculations are quite adequate for the determination of ground-state geometries and most conformational properties.[10,11]

In our calculations, the positions of the atomic centers are systematically varied until the electronic energy is minimized. For even small molecules, this would be a formidable task were it not for the availability of computer codes which compute the analytic first and second derivatives of the energy with respect to the positions of the atoms. Given these interatomic forces and force constants, highly efficient algorithms[12] have been developed for locating molecular geometries which correspond to energy minima and saddle points.

All calculations were performed with the GRADSCF program system.[12] They were performed with several different Gaussian orbital basis sets which are of increasing complexity. These include STO-3G, a minimal basis set ascribing one contracted Gaussian function per atomic orbital; 4-31G, a split-valence basis set meaning that two functions are used to describe each valence atomic orbital; and 6-31G*, a split-valence set augmented with d-type polarization functions on the carbon and the oxygen atoms.

Calculations at the SCF level using the 6-31G* basis set are known to reproduce accurately the experimental bond lengths and bond angles for molecules comprised of first-row atoms. However, such calculations are not always feasible for molecules comprising 20–40 atoms that represent segmental units of polymers. Fortunately, it has been observed that the errors in bond lengths incurred by using smaller basis sets are not large. Also, experimental bond angles tend to lie between the minimal and split valence basis set results.[13,14] Indeed, one can often obtain accurate bond angles by averaging the STO-3G and 4-31G values. For bond angles about a central O or N atom (for example, in water, methanol, and dimethyl ether), the basis set limit results lie nearly midway between the STO-3G and 4-31G values.[13] It seems that for atoms with lone pair electrons, the error introduced by using a truncated p-orbital space is nearly canceled by the error incurred by neglecting polarization functions. Based on these results, we use the average of the STO-3G and 4-31G bond angles when 6-31G* results are not available.

Results of ab Initio Calculations

The polycarbonate segmental unit is shown schematically in Figure 1a and its geometrical parameters are denoted in Figure 1b. The region around the carbonate group is represented by diphenyl carbonate (DPC) and the region around the quaternary carbon atom by 2,2-diphenylpropane (DPP). To model the polycarbonate segmental unit, therefore, calculations were performed separately on diphenyl carbonate and 2,2-diphenylpropane.

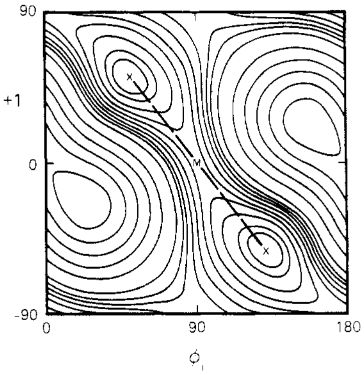


Figure 2. Conformational energy contour diagram of diphenylpropane (DPP) as function of the torsional angles of the phenylenes, ϕ_i and ϕ_{i+1} (see Figure 1a). The energies were calculated at the SCH level with the STO-3G basis set. The contour lines are drawn at energies of 0.25, 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 7.5, 10, 12.5, 15, and 17.5 kcal/mol with respect to the minima. The dashed line represents the low-energy path for the concerted phenyl motion between the skewed (X) and the Morino (M) conformations.

A. 2,2-Diphenylpropane (DPP). For DPP, the calculations were performed with STO-3G and 4-31G basis sets. The bond geometries and conformational energies show little dependence on the basis set. The supplement (θ_4) of the C^{ar}–C–C^{ar} angle changes from 70.6° in STO-3G to 70.1° in 4-31G, for example. This result is in good agreement with the experimental value of 70.5°, obtained by Perez and Scaringe[6] from the crystal structure analysis of 4,4′-isopropylidenediphenylenebis(phenyl carbonate) (DPBC).

We have computed the energy profiles along selected torsional paths by performing calculations at smoothly interpolated points connecting the optimized geometries. Furthermore, one can use a two-dimensional Fourier series to represent the complete conformational energy surface as a function of the two torsional angles of the phenylenes, ϕ_i and ϕ_{i+1}. The coefficients in the Fourier series were determined by fitting to the energies of the optimized structures, calculated at 12 selected points. The energy contour lines determined in this way by using the STO-3G basis set are shown in Figure 2.

The most stable conformation is a skewed structure denoted X in the figure with the dihedral angles (ϕ_i, ϕ_{i+1}) having values (51°, 51°). A geometrical structure having orthogonal phenyl ring planes with the dihedral angles (0°, 90°) or (90°, 0°), known as a Morino structure and denoted M, is higher in energy than the skewed structure by 1.9 kcal/mol. From Figure 2, one sees that the optimal path to change the skewed structure (X) into a Morino structure (M) follows a convoluted motion where both dihedral angles change simultaneously, as indicated by the dashed line.

B. Diphenyl Carbonate (DPC). In view of the complexity resulting from the lone-pair electrons in DPC, we first tested the level of "necessary" basis sets by checking the calculated bond angle of C^{ar}–O–C* with the experimental result. The calculations were performed on phenyl formate for this purpose and the results are listed in Table I. It is clear that the C^{ar}–O–C* angle and the phenyl rotation at the energy minimun depend strongly on the adopted basis set. In this regard, it should be noted that neither the minimal basis set STO-3G nor the next level

Table I
SCF ab Initio Calculations with Full Geometry Optimization for Phenyl Formate

basis sets	ψ, deg	θ_1, deg
STO-3G	58	65.1
4-31G	0	50.7
6-31G* (O_d)[a]	90	61.6
6-31G*[b]	64	59.5
cryst struct of DPC[15]	45	60

[a] d functions on the oxygen atoms only. [b] d functions on both the oxygen and carbon atoms.

Table II
SCF ab Initio Calculations with Full Geometry Optimization for Phenyl Formate and Monophenyl Carbonate

basis set	ψ	$E(\psi)$,[a] kcal/mol
6-31G*	64	0.0
	90	0.01
	0	0.72

basis sets	E(cis,trans)[b] − E(trans,trans)
STO-3G	1.72 (1.68)[c]
4-31G	2.97
6-31G*	2.75

[a] The calculations are for the trans conformation of phenyl formate. [b] The calculations are for monophenyl carbonate and the torsional angle ψ at the energy minimum of the cis state is 90°. [c] The value in parentheses is calculated for diphenyl carbonate.

4-31G basis set calculations leads to satisfactory results for DPC, owing to the significant contributions of the polarization functions which are neglected in these calculations. The most sophisticated 6-31G* scheme with d-functions on both carbon and oxygen atoms is required to match the experimental value, $\theta_1 = 60°$, on DPC.[15] (Perez and Scaringe obtained a value of $\theta_1 = 63°$ from the crystal structure determination of DPBC,[6] but their results may be susceptible to a larger uncertainty owing to the much more complicated geometrical analyses.)

The details of the conformational energy, thus calculated with the 6-31G* basis set for phenyl formate, are listed in Table II. In the preferred trans state of the carbonate group, the energy profile with the phenyl rotation ψ is nearly flat with the maximum barrier of only 0.72 kcal/mol when the phenyl plane is coplanar with the carbonate group ($\psi = 0$). The calculated energy difference between the cis and the trans state of the carbonate group is ca. 1.68 kcal/mol according to the STO-3G basis set calculations for diphenyl carbonate. This energy difference is found to be nearly the same, 1.72 kcal/mol, for the simpler model monophenyl carbonate in the same STO-3G scheme. Hence, the higher level 4-31G and 6-31G* calculations were then carried out only for the monophenyl carbonate due to computational limits. As shown in Table II, the calculated energy difference between the cis and trans conformations of the carbonate group in the 4-31G and 6-31G* basis sets is substantially larger than the 1.7 kcal/mol of the STO-3G calculations. The result with the 6-31G* basis set, 2.75 kcal/mol, is therefore taken to be most reliable (see below). Moreover, the energy barrier for the trans–cis transition, which is only 4.5 kcal/mol according to the STO-3G calculations, is found to be 7.7 kcal/mol with the 6-31G* basis set.

Full geometry optimization for DPC was carried out with the STO-3G basis set only. The more sophisticated 4-31G and 6-31G* calculations were performed for phenyl formate and monophenyl carbonate, however. The geometries of DPC for these basis sets were then determined by assuming that the differences from the STO-3G geometries remain the same as those for monophenyl carbonate. For this purpose, the calculations were carried out at a fixed phenylene rotation $\psi = 90°$, in view of the nearly flat energy profile with ψ. The geometric parameters other than θ_1, e.g., the lengths of C^{ar}–O and O–C* and the O–C*–O angle, do not depend substantially on the basis set, as shown by the results in Table III. Of particular interest here is that the angles C^{ar}–O–C* and O–C*–O (see the supplementary angles θ_1 and θ_2 in Table III) are more opened up by 4–5° in the cis state than in the preferred trans state. Also listed in the same table are the results from the X-ray structural analyses of DPC[15] and DPBC.[6] In general, the 6-31G* results are in excellent agreement with the experimental values. Alternatively, the averages of the STO-3G and 4-31G calculations also show good agreement with experiments.

Unperturbed Chain Dimensions

The unperturbed mean-square end-to-end distance $\langle r^2\rangle_0$ of the PC chain is calculated from the rotational isomeric state (RIS) model of Williams and Flory,[1] augmented by a more recent scheme for the matrix computations:[16]

$$\langle r^2\rangle_0 = \mathbf{Z}^{-1}\mathbf{g}_{[1}\mathbf{g}_2^{(n-2)}\mathbf{g}_{n]} \tag{1}$$

where

$$\mathbf{Z} = \mathbf{U}_1\mathbf{U}_2 \ldots \mathbf{U}_{n-1}\mathbf{U}_n \tag{2}$$

$\mathbf{U}_i = 1$ for the type-1 bonds in Figure 1b, and

$$\mathbf{U}_2 = [1 \quad \gamma] \tag{3}$$

$$\mathbf{U}_3 = \begin{bmatrix} 1 & \gamma \\ 1 & 0 \end{bmatrix} \tag{4}$$

$$\mathbf{U}_4 = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{5}$$

for the type −2, −3, and −4 bonds, respectively, where γ is the statistical weight for the cis conformation of the carbonate group. The matrices $\mathbf{g}_i$ are formulated from the

Table III
Geometrical Parameters of PC Chain Denoted in Figure 1b

			$\theta_1 = \theta_3$		θ_2		
	l_1 ($l_{C^{ar}-O}$)	l_2	trans	cis	trans	cis	θ_4
STO-3G	5.75 (1.41)	1.39	65.5	64.5	74.8	68.6	70.6
4-31G	5.71 (1.40)	1.34	56.0	53.8	72.7	69.0	70.1
av of STO-3G + 4-31G	5.73 (1.41)	1.36	60.7	59.2	73.7	68.8	70.4
6-31G*	5.73[a] (1.39)	1.32	59.5	56.8	73.5	68.3	(70.4[b])
cryst struct[c]	5.76[a] (1.42)	1.32	60		73		70.5

[a] The distance of a quaternary carbon–aromatic carbon is taken to be 1.54 Å. [b] This value of θ_4 is taken to be equal to the average of STO-3G and 4-31G results. [c] All the values except θ_4 are taken from the results of diphenyl carbonate,[15] and the θ_4 is taken from Perez and Scaringe.[6]

Table IV
Comparison of Calculated Values of $\langle r^2 \rangle_0/M$ for the PC Chain

		$\langle r^2 \rangle_0/M$		
T, K	γ	ab initio (6-31G*)	Yoon and Flory[17]	Williams and Flory[1]
0	0	1.12	1.1	0.87
300	0.01	1.11		0.86
445	0.04	1.08		0.85
750	0.16	1.00		0.83
1000	0.25	0.95		0.81

elements μ_{ij} of the statistical weight matrix $\mathbf{U}$ and the generator matrix $\mathbf{G}_i$,[16]

$$\mathbf{g}_i = \begin{bmatrix} \mu_{\alpha\alpha}\mathbf{G}(\alpha) & \mu_{\alpha\beta}\mathbf{G}(\beta) & \cdots & \cdots \\ \mu_{\beta\alpha}\mathbf{G}(\alpha) & \mu_{\beta\beta}\mathbf{G}(\beta) & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix}_i \tag{6}$$

and

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^{\mathrm{T}}\mathbf{T} & l^2 \\ 0 & \mathbf{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_i \tag{7}$$

and $\mathbf{g}_{[1}$ is the first row of $\mathbf{g}_1$ and $\mathbf{g}_{n]}$ is the last column of $\mathbf{g}_n$. The matrix $\mathbf{T}_i$ which transforms the cartesian coordinates in the $(i + 1)$th bond to those of the ith bond is defined as usual,[16]

$$\mathbf{T} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\psi & -\cos\theta\cos\psi & \sin\psi \\ \sin\theta\sin\psi & -\cos\theta\sin\psi & -\cos\psi \end{bmatrix}_i \tag{8}$$

For the type -1 and -4 bonds, the transformation matrix is simplified to $\langle \mathbf{T}(\theta_i) \rangle$ due to the twofold symmetry of the conformational energies as a function of phenyl rotations:[1]

$$\langle \mathbf{T}(\theta_i) \rangle = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}_i \tag{9}$$

Results and Discussion

The unperturbed mean-square end-to-end distances $\langle r^2 \rangle_0$ are calculated from eq 1–9, by using the bond geometries of 6-31G* except θ_4, for which the average of STO-3G and 4-31G results is used, and taking the energy difference between the cis and the trans state of the carbonate group to be 2.75 kcal/mol (see Table II). The effect of this parameter, γ, in eq 3 and 4, was explored by changing the temperatures. The results of $\langle r^2 \rangle_0/M$, M being the molecular weight, obtained for sufficiently large repeat units (>1000), are listed in Table IV. Our calculated value of $\langle r^2 \rangle_0/M$ from the ab initio method is rather insensitive to the value of γ and falls around 1.1 for a reasonable range of γ. Including errors of ±1° in each bond angle leads to a possible error of ±0.08 in our calculated value of $\langle r^2 \rangle_0/M$. Previously, Williams and Flory[1] calculated $\langle r^2 \rangle_0/M$ to be ca. 0.85 by taking θ_1 to be 67°. More recently, Yoon and Flory[17] obtained a value of ca. 1.1 using the experimentally determined values for $\theta_1 = 60°$ and $\theta_2 = 73°$ and assuming $\theta_4 = 70°$ and $\gamma = 0$.

Experimentally, Berry et al.[18] first measured $\langle r^2 \rangle_0/M = 0.87$ from the intrinsic viscosities. Recently, Gawrisch et al.[19] obtained a value of ca. 1.28 by small-angle neutron scattering (SANS) from the bulk amorphous PC at room temperature. Ballard et al.[20] measured 1.25 ± 0.05 by SANS from the bulk amorphous PC of different molecular weights.

Therefore, the value calculated from the ab initio geometries and energies in conjunction with the rotational isomeric state model is in good agreement with the experimental results for the bulk amorphous PC chain within the limit of errors. The lower experimental value obtained in dilute solutions may arise from the experimental difficulites of solubility or thermal stability that Berry et al. encountered.[18] Certainly, it will be important to establish the correct experimental value for the PC chain in Θ-solvents in this regard.

It should be pointed out that our value, 2.75 kcal/mol, for the energy difference between the trans and cis conformations of the carbonate group is substantially larger than previous estimates. Williams and Flory[1] first estimated a value of 1.3 kcal/mol from the 6-12 empirical energy functions. Tekely and Turska[3] obtained 1.8 kcal/mol from a similar empirical method. More recently, Bicerano and Clark[21] obtained a value of 1.1 kcal/mol by using the PRDDO method,[22] which is an approximate ab initio scheme simulating the minimal basis set STO-3G method. As shown in Table II, our STO-3G estimate (1.68 kcal/mol) is slightly larger than that of this approximate minimal basis set PRDDO estimate. Moreover, this value is found to increase to 2.75 kcal/mol in the most rigorous 6-31G* calculations as the contributions of the polarization functions are correctly taken into account. Hence, this cis–trans energy difference should be considerably larger than the PRDDO estimate.

Our estimate of the energy barrier for the phenyl rotations within diphenylpropane (1.9 kcal/mol) is very close to the results of the empirical calculations[2,5,6] but somewhat lower than the result of semiempirical MNDO calculations (3.3 kcal/mol) of Bendler.[7] The barrier of only 0.7 kcal/mol for the phenyl rotation ψ within DPC, obtained from our 6-31G* calculations, is much lower than the previous estimates from empirical[5] and semiempirical[8] methods. This difference is mostly attributable to the importance of taking into account the polarization functions correctly. With the 6-31G* basis set, our estimate of the trans–cis transition barrier within the carbonate moeity is ca. 7.7 kcal/mol, which is considerably larger than previous estimates. For example, Jones et al.[8] report a value of 5.3 kcal/mol from their STO-3G calculations without full geometry optimization. Our STO-3G result, which is fully optimized, is 4.5 kcal/mol. All of these are quite a bit larger than the MNDO estimate of 2.4 kcal/mol.[8]

In conclusion, it is found that the ab initio quantum mechanical calculations with 6-31G* basis sets are capable of providing detailed information on the bond geometries and the conformational energetics of the PC chain, in good agreement with available experiments. The calculated energy profiles showing relatively low barriers for all the internal rotations of phenylene groups as well as the cis–trans transition of the carbonate conformation are very likely to be a major factor in understanding the dynamical properties of PC chain. The results obtained here are also highly encouraging to motivate further applications of ab initio calculations to other polymers for which the geometries or the conformational energetics have not been determined satisfactorily through the more conventional methods.

Acknowledgment. The work of B.C.L. was supported by NASA Contract NAS2-12424. B.C.L. is also indebted for support of this work to the IBM Corporation under a Joint Study Agreement with Analatom Incoporated.

Registry No. DPC, 102-09-0; DPP, 778-22-3; $HCO_2C_6H_5$, 1864-94-4; $HO_2COC_6H_5$, 13932-55-3; bisphenol A polycarbonate (SRU), 24936-68-3; bisphenol A polycarbonate (copolymer), 25037-45-0.

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Head–Head Interactions in Zwitterionic Associating Polymers

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Received November 12, 1987

ABSTRACT: Theoretical calculations are presented, both at the molecular mechanics empirical level and at the Hartree–Fock semiempirical level (MNDO), on molecules containing (ammonioalkyl)sulfonate zwitterions as models for semitelechelic associating polymers. In particular the interactions between the zwitterionic head groups and the evolution of the energetics and structures of the molecules are examined as a function of their aggregation. The clustered zwitterions adopt an extended (all-trans) conformation with their dipoles aligning in an antiparallel fashion in order to favor interchain electrostatic interactions. For large aggregation numbers in apolar solvents, associating polymers with zwitterionic head groups are predicted to form reverse micelles that possess either a tubelike or a disklike structure. Spherical structures are not energetically favorable. The excluded-volume interaction of the long hydrocarbon tails in the semitelechic polymers is expected to favor the tubelike structure.

I. Introduction

Associating polymers[1–7] have attracted considerable interest because they exhibit a number of unique rheological properties in dilute and semidilute solutions, an example being shear thickening.[8–11] Associating polymers consist of long-chain polymers containing a small fraction of strongly associating side groups. Ionomers are one well-studied example.[1–5] Since structure–property relationships for associating polymers are not fully established, it is important to study structurally simplified materials in order to clarify some of the fundamental issues. Recently, Fetters et al.[12,13] have followed that approach and have reported the synthesis and rheological properties of "semitelechelic" polyisoprenes, where long, flexible polyisoprene chains are capped at one end by an (ammoniopropyl)sulfonate zwitterion (see Figure 1). In aliphatic hydrocarbon solvents such as cyclohexane, light-scattering, osmometry, and viscometry experiments give clear evidence of association of the zwitterion groups, i.e., for (reverse) micellization.[12] The characteristic aggregation number is typically on the order of 5–30 and depends strongly on the molecular weight of the long polyisoprene tails. The aggregation number is smaller in aromatic and moderately polar solvents and decreases rapidly with small additions of alcohol.[12]

The conformational properties of these associating polymers in *nonpolar solvents are influenced* by the competing tendencies coming on the one hand from the lipophobic associating groups which want to aggregate and on the other hand from the long hydrocarbon regions which want to avoid one another. Standard methods of polymer theory have been employed to treat the excluded-volume interaction between tails for the case of spherical clusters.[14–16] However, since there is no precise information concerning the stereochemistry of the zwitterionic head groups, it is not straightforward to formulate a good description of their aggregation. Such a description has up to now been based on rather simple models, for instance the liquid drop model,[17] which assume spherical symmetry and do not take into account the detailed nature of the head–head interactions.

Our purpose in this work is to provide some theoretical insight into the interactions between the zwitterionic head groups (energetics and structure) in order to help refine the aggregation models for this type of associating polymer. We note that the systems considered here are quite dif-

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0024-9297/88/2221-1633$01.50/0