Macromolecules 1981, *14*, 947-950

Phenylene Group Rotations and Nonplanar Conformations in Some *cis*- and *trans*-Poly(benzobisoxazoles) and -Poly(benzobisthiazoles)

W. J. Welsh, D. Bhaumik, and J. E. Mark*

Department of Chemistry and Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221. *Received November 7, 1980*

ABSTRACT: Planarity, or departures therefrom, can be of considerable importance in the formation of either crystalline or liquid-crystalline phases in rigid-rod polymeric systems. Of the four aromatic heterocyclic polymers *cis*- and *trans*-poly(benzobisoxazoles) (PBO) and -poly(benzobisthiazoles) (PBT), the *cis*-PBO and *trans*-PBT are known to form such phases, and the present investigation involves energy calculations carried out to characterize any deviations from planarity arising from *p*-phenylene group rotations along these chain backbones. Intramolecular (conformational) energy calculations indicate that the two PBO polymers should be planar, and this conclusion is in agreement with experimental results obtained on pertinent model compounds. Similar calculations on the PBT polymers correctly predict nonplanarity but overestimate its magnitude. Inclusion of intermolecular contributions (chain-packing effects) in this case considerably improves the agreement between theory and experiment.

Introduction

A number of aromatic heterocyclic polymers[1-12] have been found to have exceedingly attractive properties, including very high mechanical strength, excellent thermal stability, and unusual resistance to most common solvents. Of particular interest have been the para-catenated polymers of the type illustrated in Figure 1. The poly(benzobisoxazole) (PBO) shown here is designated the cis form on the basis of the relative locations of the two oxygen atoms in the repeat unit. Other related polymers of interest are the *trans*-PBO and the cis and trans forms of the corresponding poly(benzobisthiazole) (PBT), in which the two oxygen atoms are replaced by sulfur atoms. Chains of this type are relatively rigid and frequently form liquid-crystalline[13-19] as well as crystalline phases. In spite of the rigidity of the molecules, however, there is some conformational flexibility in that rotations should be permitted (at least to some extent) about the *p*-phenylene groups in each repeat unit. Such rotations ϕ are illustrated in the chain segment shown in Figure 2. The associated flexibility could be important with regard to solubility characteristics of the polymer and chain-packing effects in the crystalline and liquid-crystalline states.

The present theoretical investigation was undertaken in an attempt to characterize and elucidate this type of conformational flexibility in PBO and PBT polymers. Calculations of intramolecular (conformational) energies were carried out by using standard semiempirical potential energy functions, with contributions for nonbonded, torsional, and Coulombic interactions.[20,21] Of primary interest are the identification of the conformations of lowest energy and their comparison with known crystalline-state conformations of relevant model compounds.[22,23] If a predicted conformation is nonplanar, the estimated energy difference between it and the planar conformation, and the rotational energy profile in general, becomes of considerable importance. Also, in such cases the calculations will be extended to take approximate account of intermolecular interactions, which one would intuitively expect to increase the accessibility of the planar conformation.

Theory

Conformational and Intermolecular Energies. The energy calculations pertain to the chain segment shown in Figure 2 and were carried out as a function of the rotational angle ϕ. As is customary in conformational analyses,[20] $\phi = 0°$ corresponds to the coplanar conformational state, with positive values of ϕ corresponding to the direction that would advance a right-handed screw. The total energy E associated with a given conformation was considered to be the sum of the steric or van der Waals energy E_{vdW}, the torsional contribution E_{t}, and the Coulombic energy E_{C}. Interactions not dependent on ϕ are of no interest in the present calculations and were therefore not included.

The van der Waals interactions between a pair of atoms i and j separated by the distance d_{ij} were treated by using the Buckingham potential function[20]

$$E_{\mathrm{vdW}} = \sum_{i<j}[a_{ij}\exp(-b_{ij}d_{ij}) - c_{ij}/d_{ij}^{6}] \qquad (1)$$

with the parameters a, b, and c differing, of course, for different atom pairs. The parameter c characterizing the attractions was calculated from atomic polarizabilities[24] by application of the Slater–Kirkwood equation.[25] Values of b for a like atom pair were taken from Scott and Scheraga[26,27] while values for an unlike pair were given by $b_{ij} = (b_{ii}b_{jj})^{1/2}$. The corresponding values of the parameter a were then determined by minimizing eq 1 at $r_{\min} = r_1 + r_2$, where r_1 and r_2 are the van der Waals radii, taken from crystal structure data.[28] (In these calculations of conformational energies, the values of r_1 and r_2 were augmented by 0.1 Å, as suggested by Flory[20] and others.[29] The increase is introduced to compensate for the absence, in this application, of long-range attractive forces that are operative in the crystal.)

Our choices for some of the Buckingham parameters a, b, and c require additional comments. It is particularly important to distinguish between aliphatic and aromatic carbon atoms. The basis for the difference can be understood by considering two overlapping, parallel benzene molecules. Due to the presence of π-electron clouds above and below each molecule, the equilibrium intermolecular carbon-to-carbon distances are greater than they would be if the carbon atoms were aliphatic. To account for this enhanced thickness in a direction perpendicular to the plane of the ring, aromatic carbon atoms are frequently assigned a larger van der Waals radius ($r = 1.85$ Å) than the value given for an aliphatic carbon (1.70 Å).[28] However, these assignments increase the size of the carbon atom in all directions, i.e., spherically, and ignore the fact that the increase in thickness is directional. An improvement would be to regard an aromatic carbon as "aromatic" only in a direction nearly perpendicular to the ring and as

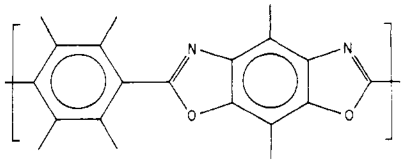

Figure 1. *cis*-PBO repeat unit.

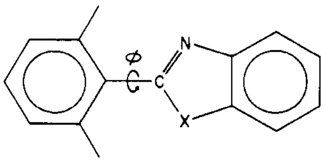

Figure 2. Rotatable segment in PBO (X = O) and PBT (X = S).

Table I
Values of the Parameters[a] for the van der Waals Interactions

atom pair	r_{min}, Å	$10^{-3}a$	b	c
C···C	3.60	908.6	4.59	363.0
C···N		755.3	4.59	445.9
C···O		432.2	4.59	275.5
C···S		1163	4.25	1158
C···H		86.10	4.57	127.0
N···H		75.43	4.57	156.0
O···H		41.75	4.57	92.2
S···H		123.3	4.22	407.0
H···H	2.60	10.37	4.54	47.1

[a] Units are such as to give E in kcal/mol when d_{ij} is in Å.

"aliphatic" in a direction more nearly parallel to the ring.[30] This was the approach taken in the present investigation. The oxygen parameters are those given for a hydroxyl oxygen in a typical organic acid.[31] This choice was based on the similarity in length of the C–O bond in such acids (1.36 Å)[32] and in the PBO model compounds (1.325 Å for cis, 1.37 Å for trans).[22,23] The nitrogen parameters are those given for a nitrogen atom in a polypeptide backbone, again based upon the similarity in the length of the C–N bond in a polypeptide (1.32 Å)[20,33] and those observed in model compounds for both PBO (1.325 Å for cis, 1.30 Å for trans)[22,23] and PBT (1.30 Å for cis, 1.292 Å for trans).[22,23] These comments pertain to the intramolecular interactions, but only slight modifications, described elsewhere,[34,35] are required for the intermolecular energy calculations. Illustrative values of the parameters for the most important case of augmented values of r_1 and r_2 and aliphatic-type carbon atoms are given in Table I.[34-37]

The torsional contributions were calculated from the standard representation[20,21]

$$E_t = (E_0/2)(1 - \cos 2\phi) \qquad (2)$$

where E_0 is the intrinsic barrier height for the specified rotation. The required value of E_0 was obtained from experimental studies of small molecules, on the perfectly reasonable assumption that such information is transferable to polymeric chains.[20]

Coulombic energies were represented by the equation[20,21]

$$E_C = \sum_{i<j} 332.072 q_i q_j / \epsilon d_{ij} \qquad (3)$$

where q_i and q_j are, respectively, the partial charges on atom i and atom j, separated by distance d_{ij}, in a medium having a bulk dielectric constant ϵ. (The conversion factor 332.072 gives E_C in units of kcal/mol when d_{ij} is in Å and q is in units of electron charge.) Since Coulombic energies are frequently of only minor importance,[37] ϵ was assigned the value unity to determine the maximum possible contribution from this source. The values of the (conformation-dependent) partial charges q were determined as a function of ϕ by the CNDO/2 (complete neglect of differential overlap) method.[38] Typical results, those calculated for the *cis*-PBO segment shown in Figure 2 (X = O), are given in Table IA (supplementary material). The Coulombic energies thus calculated for *cis*-PBO and *trans*-PBT were assumed also to apply to *trans*-PBO and *cis*-PBT, respectively.

Table II
Detailed Information on the Conformational Energies[a] of the *cis*-PBO Segment

ϕ, deg	E_{vdW}	E_t	E_C	E	d,[b] Å
0	−0.233	0.000*	−1.090	−1.32*	2.56
10	−0.009	0.139	−1.114	−0.984	2.57
20	−0.433	0.538	−1.120	−1.01	2.62
30	−0.620	1.150	−1.126	−0.596	2.68
40	−0.810	1.900	−1.165	−0.075	2.77
50	−0.960	2.699	−1.170*	0.569	2.88
60	−1.070	3.450	−1.145	1.23	2.99
70	−1.140	4.062	−1.120	1.80	3.12
80	−1.180	4.461	−1.100	2.18	3.24
90	−1.200*	4.600	−1.096	2.30	3.37

[a] Energies are in kcal/mol, with asterisks specifying minimum values. [b] Distance between the O atom and the closer phenylene H atom separated from it by four bonds (see Figure 2).

In one case, where nonplanarity was predicted, additional calculations were carried out to investigate the effect of intermolecular interactions on the rotational angle, as described elsewhere.[34,35] These calculations were based on three chain segments, each of which was assigned the same, specified value of ϕ. Different parallel arrangements of the chains at various spacings were investigated in order to find the one of lowest intermolecular energy. An entire series of calculations was carried out in this manner for ϕ varied in increments of 10°. For each value of ϕ, this approximate intermolecular contribution was added to the conformational part already calculated to give the total energy as a function of ϕ.

Structural Information. The bond lengths and bond angles of the molecular segments were those obtained in the X-ray studies of Fratini and co-workers on the PBO and PBT model compounds.[22,23] The values are typical of aromatic heterocyclic compounds, and some information of this type is cited in the preceding section. The torsional barrier E_0 was assigned the value 4.6 kcal/mol, which corresponds to that found in gaseous benzaldehyde.[39] This value is in satisfactory agreement with the values 3.7 and 4.0 kcal/mol used by Birshtein and co-workers[40] and by Flory and co-workers,[41] respectively, for similar types of bonds. As expected, the phenylene groups had perfect or near-perfect twofold symmetry. The only values of ϕ of relevance were therefore in the range 0–90°.

Results and Discussion

As described above, values were calculated for the van der Waals, torsional, and Coulombic energies and the sum of these (the total conformational energy) as a function of the rotational angle ϕ. Typical results, those for *cis*-PBO and *trans*-PBT, are given in Tables II and III, respectively. The corresponding results for *trans*-PBO and *cis*-PBT are given in Tables IIA and IIIA, respectively, as part of the supplementary material. Also included in these tables are values of the distance between the heteroatom X and the closer phenylene H atom separated from it by four bonds, as illustrated in Figure 2. The interaction between these

Table III
Detailed Information on the
Conformational Energies[a] of the *trans*-PBT Segment

ϕ, deg	E_{vdW}	E_{t}	E_{C}	E	d,[b] Å
0	4.457	0.000*	−0.508*	3.95	2.66
10	4.100	0.139	−0.500	3.74	2.68
20	3.154	0.538	−0.496	3.20	2.73
30	1.913	1.150	−0.330	2.73	2.80
40	0.672	1.900	−0.350	2.22	2.91
50	−0.376	2.699	−0.290	2.03	3.03
60	−1.154	3.450	−0.311	1.98*	3.18
70	−1.670	4.062	−0.220	2.12	3.32
80	−1.965	4.461	−0.200	2.29	3.50
90	−2.071*	4.600	−0.191	2.34	3.62

[a] Energies are in kcal/mol, with asterisks specifying minimum values. [b] Distance between the S atom and the closer phenylene H atom separated from it by four bonds (see Figure 2).

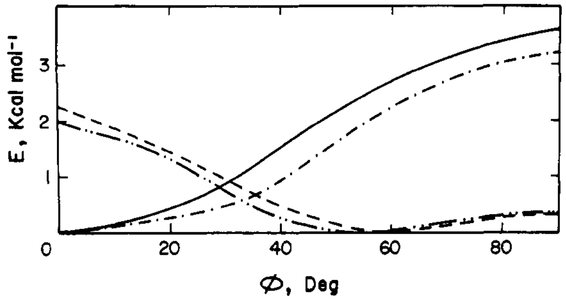

Figure 3. Conformational energy shown as a function of rotation angle for *cis*-PBO (—), *trans*-PBO (-·-), *cis*-PBT (---), and *trans*-PBT (-··). In each case, the energies are expressed relative to zero for the energy minimum.

two atoms is of considerable importance because of the possibility of steric repulsions interfering with the attainment of coplanarity between the two parts of the repeat units. This is, of course, particularly important with regard to possible differences in conformational behavior between PBO and PBT.

The most important results are summarized in Figure 3, which shows the total conformational energy as a function of ϕ for all four chains. In the case of *cis*-PBO, the lowest energy form is seen to correspond to $\phi = 0°$, and this is in excellent agreement with the planarity found for the corresponding model compound in the crystalline state.[22] *trans*-PBO is also predicted to be planar, as one might anticipate, and preliminary results[22] are consistent with this expectation.

Significant nonplanarity is predicted for *trans*-PBT, with ϕ estimated to be approximately 55°. The nonplanarity predicted for the PBT, but not for the PBO polymers, is due to the fact that the S atom has a much larger van der Waals radius than the O atom (~1.85 vs. 1.40 Å).[20,28] Since the van der Waals radius of an H atom is ~1.15 Å, repulsions should become important when the smaller phenylene H···O distance becomes significantly less than 2.55 Å or the corresponding H···S distance less than 3.00 Å. As shown in Tables II and IIA, this H···O separation in the planar conformation of *cis*-PBO and *trans*-PBO is almost exactly this critical value of 2.55 Å. The corresponding separation in *trans*-PBT is 2.66 Å, which is ~0.34 Å less than the critical value of 3.00 Å.

The pertinent experimental ϕ value, obtained from a crystalline *trans*-PBT model compound, is 23.2°.[22,23] The lack of quantitative agreement between theoretical and experimental results is less significant than the numerical differences in ϕ might suggest. First, the energy changes only gradually with ϕ near the minimum; specifically, the entire range $\phi = 25$–$90°$ gives energies within 1 kcal/mol of the minimum value, and this indicates considerable rotational flexibility. Second, the torsional barrier $E_0 = 4.6$ kcal/mol chosen in these calculations may underestimate the true barrier to rotation. In the rigid-rod polymer, the coplanar conformation may be favored by long-range resonance stabilization which is absent in benzaldehyde, the model compound used for the estimate of E_0. Some evidence for this possibility exists in that the length of this bridging bond in the polymers of interest is 1.46 Å, which is smaller than the lengths of corresponding bonds in analogous low molecular weight species,[32] such as benzoic acid (1.49 Å), diethyl terephthalate (1.48 Å), and benzamide (1.50 Å). The smaller bond length in PBO and PBT does suggest some partial double-bond character in these C–C bonds. Third, and possibly most important, the discrepancy between theory and experiment in this case could be due to intermolecular forces, which could strongly favor a more nearly planar conformation for more efficient chain packing. The effect of including intermolecular interactions in the total energy is shown in Figure 4. Although these results are extremely approximate, it is important to note that this combined energy does show a broad minimum between $\phi \simeq 0°$ and $\phi \simeq +25°$, a region which includes the experimentally observed angle of ~23°.[22,23] These results strongly suggest that intermolecular interactions can have a significant effect on chain conformation.

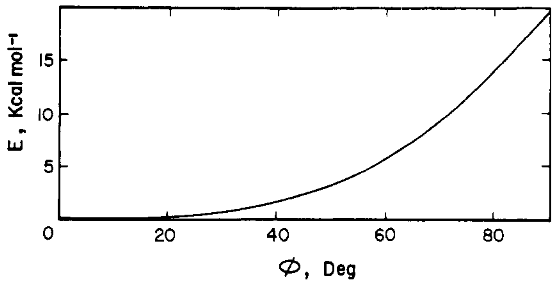

Figure 4. Sum of the conformational energy and an estimate of the intermolecular interaction energy for *trans*-PBT shown as a function of the rotation angle.

The *cis*-PBT chain is also predicted to be significantly nonplanar, but the experimental results[22,23] indicate a deviation of only 2.8–5.8° from planarity. Molecules of this type are much more complicated than the three others in that they have considerable "bowing" within the repeat unit, presumably due to strain arising from the S atoms located cis to one another.[23] In any case, calculations of conformational and intermolecular energy are greatly complicated by this bowing[23] and will therefore have to be the subject of a separate theoretical investigation.

The conformational energy profiles shown in Figure 3 indicate that the phenylene groups in the PBT chains should have somewhat greater flexibility than those in the PBO chains. This could be of importance with regard to the properties of these chains in solution and in the liquid-crystalline state. The results also furnish information concerning the nature of the barriers to rotation. For both the *cis*-PBO and *trans*-PBO segments, the torsional term dominates in that it shows the greatest change over the range $\phi = 0$–$90°$; the change in E_{t} is 4.6 kcal/mol compared with 1.20 kcal/mol for E_{vdW} and 0.09 kcal/mol for E_{C}. However, for the *cis*-PBT and *trans*-PBT segments, E_{vdW} makes the largest contribution. The changes are 6.5–6.9 kcal/mol for E_{vdW} compared with 4.6 kcal/mol for E_{t} and 0.32 kcal/mol for E_{C}. The differences can be traced to the larger size of the S atom in the case of repulsions occurring at small distances of separation and to higher polarizability[37] in the case of attractions at larger distances. It is also interesting to note that Coulombic interactions are not very important with regard to the conformational energy. Since they are also relatively unimportant with regard to interchain interactions,[35] these observations suggest that the dielectric constant of a solvent should have relatively little effect on this type of rotational flexibility. Protonation of the chain, however, would be expected to have an effect,[42] as could also any "specific solvent interaction"[43-45] with the chain segments.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Grant AFOSR 78-3683, Chemical Structures Program, Division of Chemical Sciences). We also acknowledge, with gratitude, the very useful information, help, and advice provided by Professors A. V. Fratini of the University of Dayton, P. J. Flory of Stanford University, and H. H. Jaffé of The University of Cincinnati.

Supplementary Material Available: Partial charges for the *cis*-PBO segment and detailed conformational energy information on *trans*-PBO and *cis*-PBT (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Berry, G. C. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (1), 146.
(2) Wong, C.-P.; Ohnuma, H.; Berry, G. C. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (1), 167.
(3) Wolfe, J. F.; Arnold, F. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (2), 414 and pertinent references cited therein.
(4) Berry, G. C. *J. Polym. Sci., Part C* **1978**, *65*, 143.
(5) Wong, C.-P.; Ohnuma, H.; Berry, G. C. *J. Polym. Sci., Part C* **1978**, *65*, 173.
(6) Helminiak, T. E. *Prepr., Am. Chem. Soc., Div. Org. Coat. Plast.* **1979**, *40*, 475.
(7) Husman, G.; Helminiak, T.; Adams, W. *Prepr., Am. Chem. Soc., Div. Org. Coat. Plast.* **1979**, *40*, 797.
(8) Berry, G. C.; Metzger, P. C.; Venkatraman, S.; Cotts, D. B. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (1), 42.
(9) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (1), 82.
(10) Arnold, C., Jr. *J. Polym. Sci., Part D* **1979**, *14*, 265.
(11) Wolfe, J. F.; Arnold, F. E. *Macromolecules*, this issue.
(12) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules*, this issue.
(13) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 60, 73.
(14) Flory, P. J. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 885.
(15) Flory, P. J.; Abe, A. *Macromolecules* **1978**, *11*, 1119. Abe, A.; Flory, P. J. *Ibid.* **1978**, *11*, 1122. Flory, P. J.; Frost, R. S. *Ibid.* **1978**, *11*, 1126. Frost, R. S.; Flory, P. J. *Ibid.* **1978**, *11*, 1134. Flory, P. J. *Ibid.* **1978**, *11*, 1138, 1141.
(16) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 289, 311.
(17) Wee, E. L.; Miller, W. G. *J. Phys. Chem.* **1971**, *75*, 1446. Rai, J. H.; Miller, W. G. *Ibid.* **1972**, *76*, 1081. Miller, W. G.; Rai, J. H.; Wee, E. L. *Liq. Cryst. Ordered Fluids* **1974**, *2*. Miller, W. G. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (1), 173.
(18) Berry, G. C.; Wong, C.-P.; Venkatraman, S.; Chu, S.-G. Air Force Technical Report AFML-TR-79-4115. Berry, G. C.; Casassa, E. F.; Metzger, P.; Venkatraman, S. AFML-TR-78-164, Part II.
(19) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 683. *Ibid.* **1980**, *18*, 1303, 1439. *Macromolecules* **1979**, *12*, 94, 537. *Polymer* **1980**, *21*, 21. Aharoni, S. M.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 321. *Macromolecules* **1979**, *12*, 271.
(20) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969.
(21) Hopfinger, A. J. "Conformational Properties of Macromolecules; Academic Press: New York, 1973.
(22) Wellman, M. W.; Adams, W. W.; Wiff, D. R.; Fratini, A. V. Air Force Technical Report AFML-TR-79-4184, Part I. Private communications.
(23) Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Wiff, D. R.; Fratini, A. V. *Macromolecules*, this issue.
(24) Ketelaar, J. A. A. "Chemical Constitution"; Elsevier: New York, 1958.
(25) Pitzer, K. S. *Adv. Chem. Phys.* **1959**, *2*, 59.
(26) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1965**, *42*, 2209.
(27) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *45*, 2091.
(28) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(29) Allinger, N. L.; Miller, M. A.; Catledge, F. A.; Hirsch, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.
(30) Flory, P. J., private communications.
(31) Momany, F. A.; Carruthers, L. M.; McGuire, R. F.; Scheraga, H. A. *J. Phys. Chem.* **1974**, *78*, 1595.
(32) Bowen, H. J. M.; Sutton, L. E., Eds. "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1958.
(33) Brant, D. A.; Miller, W. G.; Flory, P. J. *J. Mol. Biol.* **1967**, *23*, 47.
(34) Welsh, W. J.; Bhaumik, D.; Mark, J. E. Air Force Technical Report AFML-TR-78-3683. *J. Macromol. Sci., Phys.*, in press.
(35) Bhaumik, D.; Welsh, W. J.; Jaffé, H. H.; Mark, J. E. *Macromolecules*, this issue.
(36) Welsh, W. J.; Mark, J. E.; Riande, E. *Polym. J.* **1980**, *12*, 467.
(37) Bhaumik, D.; Mark, J. E. *Macromolecules* **1981**, *14*, 162.
(38) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.
(39) Fateley, W. G.; Harris, R. K.; Miller, F. A.; Witkowski, R. E. *Spectrochim. Acta* **1965**, *21*, 231.
(40) Zubkov, V. A.; Birshtein, T. M.; Milevskaya, I. S. *Vysokomol. Soedin., Ser. A* **1975**, *17*, 1955 (translated in *Polym. Sci. USSR (Engl. Transl.)* **1975**, *17* (9), 2252).
(41) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479. Hummel, J. P.; Erman, B.; Flory, P. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (1), 74.
(42) Thomas, E. L., private communication.
(43) Dondos, A.; Benoit, H. *Macromolecules* **1971**, *4*, 279.
(44) Yu, C. U.; Mark, J. E. *Macromolecules* **1974**, *7*, 229.
(45) Pratt, L. R.; Hsu, C. S.; Chandler, D. *J. Chem. Phys.* **1978**, *68*, 4202.