J. Phys. Chem. A **1998,** *102,* 1200−1208

United Atom Force Field for Molecular Dynamics Simulations of 1,4-Polybutadiene Based on Quantum Chemistry Calculations on Model Molecules

Grant D. Smith*

Department of Materials Science and Engineering and Department of Chemical and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112

Wolfgang Paul

Institut für Physik, Johannes Gutenberg Universität, D-55099 Mainz, Germany

Received: September 22, 1997; In Final Form: November 26, 1997

We present a united atom force field for simulations of 1,4-polybutadiene based on ab initio quantum chemistry calculations on model molecules. The geometries and energies of conformers and rotational energy barriers in model alkenes and dienes have been determined from high-level quantum chemistry calculations. A rotational isomeric state (RIS) model for 1,4-polybutadiene based on the conformer geometries and energies of the model molecules has been derived. The characteristic ratio and its temperature dependence for *cis*-1,4-polybutadiene and *trans*-1,4-polybutadiene, and the characteristic ratio of a random copolymer of cis and trans units, as predicted by the RIS model, are in good agreement with experimental values, thereby supporting the accuracy of the quantum chemistry calculations. Torsional potentials for the united atom force field have been parametrized to reproduce the quantum chemistry conformer energies and rotational energy barriers for rotations about the C(sp^2)−C(sp^2), C(sp^2)−C(sp^3), and C(sp^3)−C(sp^3) dihedrals for the model compounds. The CH_2-CH_2 united atom nonbonded potential has been taken from previous work on polyethylene melts, while the CH−CH united atom nonbonded potential has been parametrized so as to reproduce the energies of those conformers of the model molecules involving conformation-dependent second-order interactions. Finally, NPT molecular dynamics simulations have been performed on a melt of 1,4-poly(*cis*$_{0.5}$-*r*-*trans*$_{0.5}$-butadiene), and the CH_2-CH nonbonded potential has been adjusted so that the experimental melt density of the polymer as a function of temperature is accurately reproduced.

Introduction

The dynamics and relaxational behavior of 1,4-polybutadiene have been the subject of extensive experimental study in recent years. Polybutadiene is a good glass former, and its simple chemical structure, narrow molecular weight distribution, and wide variety of available microstructures, which can be controlled through adjustment of solvent, polar modifiers, and temperature during anionically initiated polymerization,[1] make it ideal for investigations of the glass transition as well as subglass and high-temperature relaxations.

Dielectric spectroscopy,[2,3] NMR spin−lattice relaxation,[4,5] and neutron scattering methods[3,6−12] have been applied in the study of polybutadiene glasses and melts. These dynamic spectroscopic techniques are the fundamental experimental probes of molecular motions because they either directly measure microscopic correlations or measure macroscopic properties directly related to microscopic correlations. These experiments have provided important phenomenological insight into the dynamic processes in polybutadiene. However, they cannot directly tell us about the fundamental chain motions leading to the observed relaxation behavior. Only through comparison with theory or simulation can such mechanistic detail be gleaned. Molecular dynamics simulations are particularly powerful in providing this mechanistic detail. We have demonstrated the ability of comparisons of experiment and molecular dynamics simulations performed on the same material under the same thermodynamic conditions to lead to important insights into the molecular motions responsible for relaxation processes in polymer melts.[13−17] Fundamental to the success of these studies were potential energy functions that faithfully reproduced conformational energies and intermolecular interactions.

In addition to extensive experimental and theoretical studies, polybutadiene melts have been the subject of several molecular dynamics simulations.[18−23] In these studies, both macroscopic (volume relaxation) and microscopic (conformational) dynamic processes have been studied. However, to our knowledge no effort has been made to compare the microscopic dynamics and relaxational behavior observable in the bulk simulations with the vast amount of experimental data available for these polymers. Our intention is to make quantitative comparisons of these properties by performing extensive molecular dynamics simulations of polybutadiene as a function of temperature and microstructure using an accurate force field based on quantum chemistry calculations on model compounds.

This paper is organized as follows. First, we report on the results of our quantum chemistry studies of the model molecules. Then, to gain additional insight into the conformational characteristic of the model molecules and corresponding polymers, we develop a rotational isomeric state (RIS) model for 1,4-polybutadiene based on the computed geometries and conformational energies for the model molecules. By comparing predictions of polymer properties from the RIS model with experiment, we attempt to better establish the accuracy of the

S1089-5639(97)03085-5 CCC: $15.00

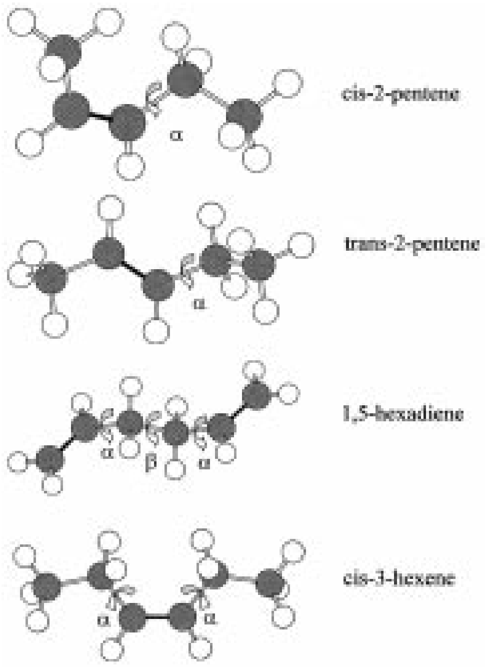


Figure 1. Structure of the primary model compounds for 1,4-polybutadienes. Conformational degrees of freedom are labeled.

quantum chemistry calculations. A comparison with previous RIS models is also undertaken. Next, we describe parametrization of a united atom force field and make some comparisons with force fields used in previous simulations of 1,4-polybutadiene. Finally, we compare predicted PVT properties for 1,4-polybutadiene from molecular dynamics simulations with experiment.

Quantum Chemistry Calculations

Conformational dynamics are fundamental to most, if not all, relaxation processes in polymers. In 1,4-polybutadienes, conformational dynamics involve rotations about allyl $CH{=}CH{-}CH_2{-}CH_2$ (α) bonds and $CH{-}CH_2{-}CH_2{-}CH$ (β) bonds. A major component of our force field parametrization effort involves obtaining accurate energies for conformers and rotational energy barriers for these dihedrals and then representing these energies with classical, atomistic potential energy functions. As model compounds for investigating rotations about the α bond we have chosen *cis*-2-pentene and *trans*-2-pentene. For rotations about the β bonds, and for correlations between the α and β bonds, we have investigated 1,5-hexadiene. For possible coupling effects across a cis double bond we have investigated *cis*-3-hexene. These compounds are illustrated in Figure 1.

Previous quantum chemistry studies of the energetics of allyl bond rotations have concentrated on 1-butene[24−26] and substituted 1-butene,[25−27] including *trans*-2-pentene.[25] For the latter, only the skew-cis energy difference was determined. In these studies, geometry optimizations were performed at the SCF level with 6-31G* or smaller basis sets, and energy calculations were performed at MP3, MP2, and SCF levels with 6-31G* or smaller basis sets. We could find no studies of the conformational energies in *cis*-2-pentene, 1,5-hexadiene, or *cis*-3-hexene.

In a recent study of *n*-butane and *n*-hexane,[28] we demonstrated that inclusion of electron correlation effects in geometry optimizations is important in obtaining accurate geometries and energies for conformers and rotational energy barriers in simple hydrocarbons. While we found that reasonably accurate values of conformer energies could be obtained with modest basis sets, such as 6-31G*, accurate values for the rotational energy barriers required additional diffuse and polarization functions in the atomic basis sets. We showed that quite accurate geometries and energies for conformers and rotational energy barriers in *n*-alkanes (conservatively, ±0.2 and ±0.5 kcal/mol for conformers and barriers, respectively) are obtained at the MP2/6-311G** level. Consequently, we have performed our quantum chemistry energy/geometry calculations on the polybutadiene model compounds at the MP2/6-311G**//MP2/6-311G** level. These calculations were performed using the quantum chemistry package Gaussian 94.[29]

The conformer and rotational barrier geometries for the model compounds are summarized in Table 1, and the relative conformer energies are summarized in Table 2. The conformational energy as a function of the α dihedral for the 2-pentene compounds and for the β dihedral in $s^+\beta s^+$ conformations of 1,5-hexadiene is shown in Figures 2−4. (See footnotes of Table 1 for conformer designations.) In addition to the saddle points tabulated in Table 1, these figures also show results of quantum chemistry optimizations obtained with constrained dihedral angles for the α (2-pentene) and β (1,5-hexadiene) bonds.

Comparison of calculated relative conformer energies and rotational energy barriers with experiment is useful for establishing the accuracy of the quantum chemistry calculations. We have made extensive comparisons of this kind for *n*-alkanes.[28] In contrast to *n*-alkanes, the conformational energetics of simple alkenes have been the subject of only limited experimental investigation. From the temperature dependence of the IR spectrum of 1,5-hexadiene, Tosi and Ciampelli[30] have estimated the gauche state of the β bond to be about 0.2 kcal/mol higher in energy than the trans state. This is in quite good agreement with our quantum chemistry energies for the $s^+g^\pm s^+$ conformers of 1,5-hexadiene (see also the RIS analysis below). We could find no experimental data for 2-pentene. For 1-butene, values of 1.60 kcal/mol[31] and 2.12 kcal/mol[32] have been reported for the t (or $s^+\_s^-$) barrier relative to the skew conformer. Experimental estimates of 0.15 kcal/mol[31] and −0.43 kcal/mol[32] have been reported for the energy of the cis conformer in 1-butene. For the purpose of comparison with these data, we performed MP2/6-311G**//MP2/6-311G** calculations on 1-butene. We obtain energies of 0.41 and 2.36 kcal/mol for the cis conformer and t (or $s^+\_s^-$) barrier, respectively. Given the paucity of experimental data and the large discrepancy between the few reported values, the most that can be said is that the quantum chemistry energies are consistent with experiment. For 1-butene we also investigated the influence of higher levels of electron correlation treatment on relative conformer energies using the MP2/6-311G** geometries. We found almost no change in the cis energy and a slight lowering of the t barrier compared to the MP2 energies. For example, the CCSD(T) energies are 0.38 and 2.09 kcal/mol for the cis conformer and t barrier, respectively.

Rotational Isomeric State Analysis of Model Compounds

It is instructive to consider the relative conformer energies for the model compounds to be the sum of conformation-dependent interactions depending on single torsions (first-order), consecutive pairs of torsions (second-order), and higher order interactions. Such a rotational isomeric state (RIS) analysis is useful in gaining greater insight into conformation-dependent interactions in these molecules. Additionally, the RIS representation of the model compounds can be extended to 1,4-polybutadiene homopolymers (trans or cis) and copolymers and

TABLE 1: Model Molecule Conformer and Barrier Geometries from Quantum Chemistry and Force Field Calculations

	dihedral angles[b,c]			valence angles[c]				bond lengths (Å)[c]				
conformation[a]	α_1	β	α_2	θ_1	θ_2	θ_3	θ_4	r_1	r_2	r_3	r_4	r_5
cis-2-Pentene												
s^+	110.7			127.4	127.6	111.5		1.501	1.344	1.501	1.532	
t (or $s^+\_s^-$)	180.0			125.4	125.7	112.1		1.502	1.343	1.513	1.530	
cis	0.0			131.3	133.1	119.5		1.505	1.346	1.509	1.528	
g (or $s^+_$cis)	17.1			130.9	132.6	119.1		1.504	1.346	1.510	1.530	
trans-2-Pentene												
s^+	116.5			124.6	124.7	111.9		1.500	1.341	1.500	1.532	
t (or $s^+\_s^-$)	180.0			124.5	124.8	112.3		1.502	1.341	1.513	1.530	
cis	0.0			130.0	126.3	115.3		1.501	1.341	1.504	1.525	
g (or $s^+_$cis)	52.2			124.3	124.6	113.3		1.502	1.342	1.513	1.533	
1,5-Hexadiene												
s^+ts^+	115.4	177.4	115.4	124.3	111.9	111.9	124.3	1.340	1.501	1.541	1.501	1.340
$s^+g^-s^+$	119.5 (116.7)	−62.2	119.5 (116.7)	124.6	112.0	112.0	124.6	1.340	1.501	1.542	1.501	1.340
$s^+g^+s^+$	109.2 (116.3)	60.3	109.2 (116.3)	124.0	112.7	112.7	124.0	1.341	1.502	1.544	1.502	1.341
$s^+(t\_g^+)s^+$	117.3	117.8	117.3	124.6	112.6	112.6	124.6	1.340	1.501	1.557	1.501	1.340
$s^+(t\_g^-)s^+$	114.2	−122.4	114.2	124.3	111.7	111.7	124.3	1.340	1.501	1.559	1.501	1.340
s^+ciss$^+$	120.3 (117.2)	−0.2	120.3 (117.2)	124.1	114.5	114.5	124.1	1.340	1.504	1.563	1.504	1.340
s^+tcis	116.2	−178.9	1.22	124.3	111.5	111.5	126.0	1.340	1.501	1.532	1.506	1.340
s^+g^+cis	119.5 (116.3)	70.0	11.2 (5.8)	123.7	112.6	115.7	126.5	1.340	1.503	1.535	1.507	1.341
s^+g^-cis	133.4 (119.5)	−68.5 (−71.5)	-6.2	124.9	113.3	116.1	126.3	1.340	1.504	1.533	1.506	1.340
cisg$^+$cis	0.5 (5.2)	73.0 (75.4)	0.5 (5.2)	126.3	116.3	116.3	126.3	1.340	1.507	1.529	1.507	1.340
cis-3-Hexene												
s^+s^+	107.9		107.9	111.6	126.9	126.9	111.6	1.535	1.503	1.346	1.503	1.535
s^+s^-	113.1		−113.1	111.4	127.4	127.4	111.4	1.535	1.503	1.346	1.503	1.535
s^+t	114.2		180.0	111.5	125.5	125.5	112.1	1.535	1.502	1.344	1.513	1.530
tt	180.0		180.0	112.6	124.1	124.1	112.6	1.529	1.509	1.344	1.509	1.529

[a] t = trans (180°), $g^\pm$ = gauche (±60°), cis = (0°), $s^\pm$ = skew (anticlinal) (±120°). Underscore indicates a saddle point between the connected conformations. [b] From quantum chemistry calculations. When force field values differ by more than 2° from the quantum chemistry values, the former are given in parentheses. [c] Bonds, valence angles, and torsional angles involving carbon atoms, delineated from left to right according to the orientations given in Figure 1.

hence allows calculation of conformation-dependent polymer properties that can be compared with experiment as a test of the accuracy of the quantum chemistry geometries and energies.

In Table 3 we present a second-order RIS representation of the conformers of 2-pentene and 1,5-hexadiene we have investigated. The 2-pentene conformer energies involve only first-order interactions, i.e., only those interactions dependent upon the conformation of the α bond. Thus we obtain $E_{\chi\mathrm{T}} = 0.5$ kcal/mol and $E_{\chi\mathrm{C}} = 4.0$ kcal/mol from the energies of the cis conformer of *trans*-2-pentene and *cis*-2-pentene, respectively. The *cis*-2-pentene trans conformation does not correspond to a relative minimum, but is actually a low-lying saddle point between the very broad skew (s^+ and s^-) minima of the α bond, as shown in Figure 2. As was done in previous RIS models for *cis*-1,4-polybutadiene,[33,34] we have assigned a rotational isomeric state to this conformation in order to account for the small but important population of the α dihedral near 180°. Based on the quantum chemistry conformational energies we assign $E_\mathrm{T} = 1.0$ kcal/mol. A nonunity preexponential factor for this state is discussed below.

Examination of the $s^+\beta s^+$ conformers of 1,5-hexadiene allows us to assign energies to the first-order interactions involved with rotations about the β dihedral. Based on the energies of the $s^+g^\pm s^+$ conformers, we assign $E_\sigma = 0.1$ kcal/mol. The remaining 1,5-hexadiene conformers allow us to investigate second-order interactions involving coupling between the α and β dihedrals. We assign an additional second-order energy $E_\psi = 0.5$ kcal/mol to $g^\pm$cis ($\beta\alpha$) sequences. Examination of Table 3 indicates good agreement between the second-order RIS model and quantum chemistry for all conformers except the cisg$^\pm$cis. As was found in previous molecular mechanics calculations,[34] our quantum chemistry calculations indicate that interactions in this conformer are better represented as $\sigma + 2\chi_\mathrm{T} + \psi$ than $\sigma + 2\chi_\mathrm{T} + 2\psi$ as predicted by the second-order model. By extending the RIS model to third-order in order to account for this effect, we obtain a good representation of this conformer.

RIS Predictions for 1,4-Polybutadiene

A review of RIS models for 1,4-polybutadiene can be found in ref 35. While a fair number of models have been proposed for this polymer, the vast majority of these are based on the models of Flory et al.[34] and Mark[33,37] with minor variations in the energy parameters. Therefore, in our development of a quantum chemistry based RIS model for 1,4-polybutadiene, and in comparison with previous models, we will emphasize these models.

In their RIS models for *trans*-1,4-polybutadiene, Flory et al.[34] and Mark[37] both assumed that no important coupling of conformations occurs across a trans double bond. However, the models differ in this respect for *cis*-1,4-polybutadiene. Here, Mark[33] assumed strong coupling between pairs of α bonds in the trans conformation, as illustrated with *cis*-3-hexene in Figure 1. To investigate possible coupling effects across a cis double bond, we performed MP2/6-311G**//MP2/6-311G** calculations on selected conformations of *cis*-3-hexene. Geometries

TABLE 2: Model Molecule Conformer and Barrier Energies from Quantum Chemistry and Force Field Calculations

	quantum chemistry		relative energy (kcal/mol)	
conformation[a]	SCF	MP2		force field
		cis-2-pentene		
s^+	0.00	0.00		0.00
t (or s^+_s^-)	0.96	1.05		1.06
cis	4.13	4.03		4.09
g (or s^+_cis)	4.32	4.14		4.16
		trans-2-pentene		
s^+	0.00	0.00		0.00
t (or s^+_s^-)	2.25	2.45		2.45
cis	0.88	0.61		0.60
g (or s^+_cis)	2.71	2.12		2.12
		1,5-hexadiene		
s^+ts^+	0.00	0.00		0.00
$s^+g^-s^+$	1.02	0.03		0.17
$s^+g^+s^+$	1.11	0.22		0.25
s^+(t_g^+)s^+	3.73	3.52		3.37
s^+(t_g^-)s^+	4.01	3.50		3.33
s^+ciss$^+$	5.48	4.43		4.65
s^+tcis	0.88	0.57		0.58
s^+g^+cis	2.27	1.03		1.34
s^+g^-cis	2.63	1.22		1.35
cisg$^+$cis	3.62	1.61		2.19
		cis-3-hexene		
s^+s^+	0.00	0.00		
s^+s^-	-0.04	0.10		
st	0.92	1.18		
tt	1.82	2.23		

[a] See Table 1 footnotes for definitions of conformers.

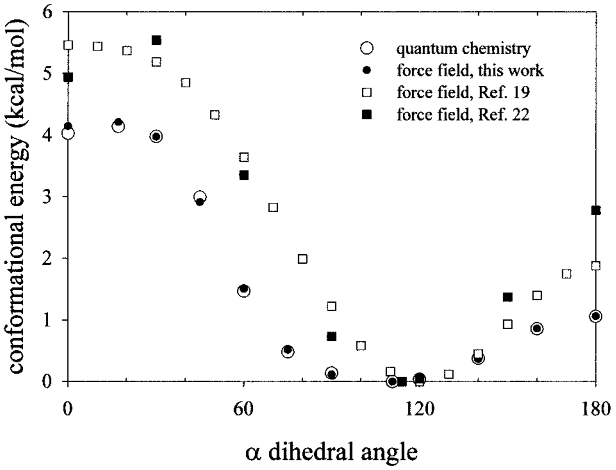


Figure 2. Conformational energy in *cis*-2-pentene as a function of the α dihedral angle.

and energies are given in Tables 1 and 2. It can be seen that the energy of the (αα) tt conformation is just twice that of s$^\pm$t, indicating no important coupling in the tt conformer. Consequently, we followed the general procedure outlined by Flory et al.[34] in the development of the statistical weight matrices described below. In addition, it is worth noting that *cis*-3-hexene s$^\pm$α conformer energies are quite similar to those for the corresponding α conformation of *cis*-2-pentene.

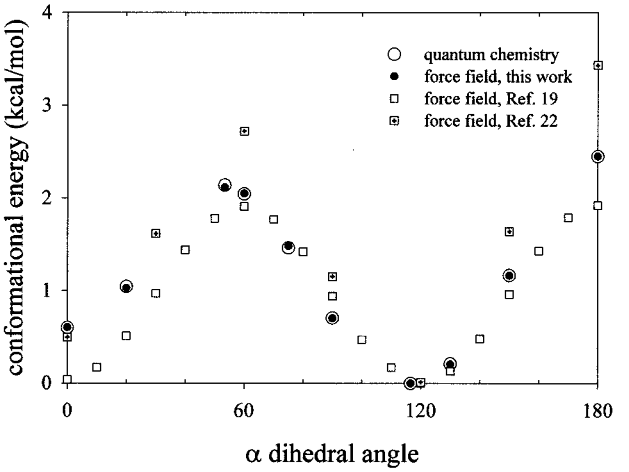


Figure 3. Conformational energy in *trans*-2-pentene as a function of the α dihedral angle.

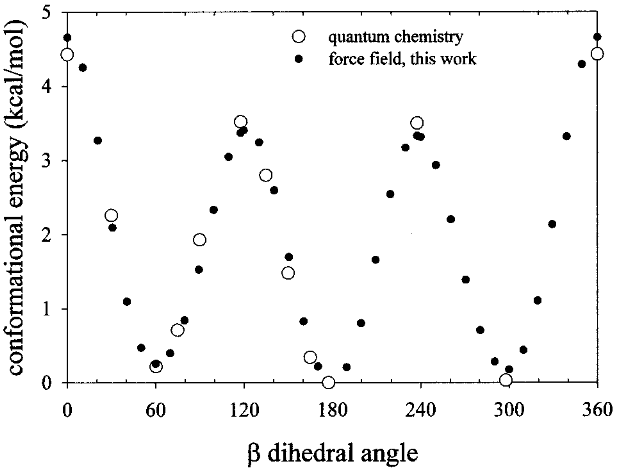


Figure 4. Conformational energy in s$^+\beta$s$^+$ 1,5-hexadiene as a function of the β dihedral angle.

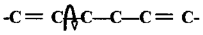
TABLE 3: RIS Representation of Model Molecule Conformations

			energy (kcal/mol)	
compound	conformer	RIS representation	RIS	q.c.
cis-2-pentene	$s^\pm$	0	0.0	0.0
cis-2-pentene	cis	χ_C	4.0	4.0
cis-2-pentene	t (s^+_s^-)	τ	1.0	1.0
trans-2-pentene	$s^\pm$	0	0.0	0.0
trans-2-pentene	cis	χ_T	0.5	0.6
1,5-hexadiene	s^+ts^+	0	0.0	0.0
1,5-hexadiene	$s^+g^-s^+$	σ	0.1	0.03
1,5-hexadiene	$s^+g^+s^+$	σ	0.1	0.22
1,5-hexadiene	$s^\pm$tcis	χ_T	0.5	0.57
1,5-hexadiene	s^+g^+cis	$\sigma + \chi_T + \psi$	1.1	1.0
1,5-hexadiene	s^+g^-cis	$\sigma + \chi_T + \psi$	1.1	1.2
1,5-hexadiene	cisg$^\pm$cis	$\sigma + 2\chi_T + 2\psi$	2.1	1.6
1,5-hexadiene[a]	cisg$^\pm$cis	$\sigma + 2\chi_T + \psi$	1.6	1.6

[a] Third-order representation.

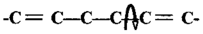
The second-order statistical weight matrices for *cis*-1,4-polybutadiene and *trans*-1,4-polybutadiene, based on the RIS analysis of the model compounds given above, are given in Table 4. The energy and geometry parameters, based on the quantum chemistry calculations on model compounds, are given in Table 5. Also shown for comparison are the values from the model of Flory et al.[34] For the trans state of the α bond, introduced into the model to account for the conformer population near 180°, the partition function as given by the quantum chemistry conformational energies shown in Figure 2 yields a preexponential factor of approximately 0.7 for the statistical weight of this state. For all other states, a preexponential factor of unity was employed. Using standard matrix multiplication methods,[36] we have calculated the characteristic ratio and its temperature dependence for *cis*-1,4-polybutadiene,

TABLE 4: Second-Order Statistical Weight Matrixes for 1,4-Polybutadiene

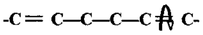


	cis	s$^+$	t	s$^-$
t	$\chi_T, \chi_T, 0, 0$[a]	1, 1, 0, 0	0, 0, 0, 0	1, 1, 0, 0
cis	$0, 0, \chi_C, \chi_C$	0, 0, 1, 1	T, T, 0, 0	0, 0, 1, 1

	t	g$^+$	g$^-$
cis	1, 1, 1, 1	$\sigma\psi, \sigma\psi, \sigma\psi, \sigma\psi$	$\sigma\psi, \sigma\psi, \sigma\psi, \sigma\psi$
s$^+$	1, 1, 1, 1	$\sigma, \sigma, \sigma, \sigma$	$\sigma, \sigma, \sigma, \sigma$
t	0, 0, 1, 1	$0, 0, \sigma, \sigma$	$0, 0, \sigma, \sigma$
s$^-$	1, 1, 1, 1	$\sigma, \sigma, \sigma, \sigma$	$\sigma, \sigma, \sigma, \sigma$



	cis	s$^+$	t	s$^-$
t	$\chi_T, \chi_C, \chi_T, \chi_C$	1, 1, 1, 1	0, T, 0, T	1, 1, 1, 1
g$^+$	$\chi_T\psi, \chi_C\psi, \chi_T\psi, \chi_C\psi$	1, 1, 1, 1	0, T, 0, T	1, 1, 1, 1
g$^-$	$\chi_T\psi, \chi_C\psi, \chi_T\psi, \chi_C\psi$	1, 1, 1, 1	0, T, 0, T	1, 1, 1, 1



	t	c
cis	1, 0, 1, 0	0, 1, 0, 1
s$^+$	1, 0, 1, 0	0, 1, 0, 1
t	0, 0, 0, 0	0, T, 0, T
s$^-$	1, 0, 1, 0	0, 1, 0, 1

[a] Statistical weights for the trans−trans, trans−cis, cis−trans and cis−cis dyads.

TABLE 5: RIS Energy and Geometry Parameters for 1,4-Polybutadiene

parameter	value (kcal/mol, Å, or deg) this work	value (kcal/mol, Å, or deg) Flory et al. (ref 34)
E_σ	0.1	0.0
$E_{\chi T}$	0.5	0.3
$E_{\chi C}$	4.0	infinity
E_T[a]	1.0 (0.7)	0.7 (0.3)
E_ψ	0.5	2.0
Bond Lengths		
CH═CH	1.34	1.34
$CH-CH_2$	1.51	1.51
CH_2-CH_2	1.54	1.53
Bond Angles		
$CH-CH_2-CH_2$	112.0	112.0
$CH=CH-CH_2$ trans[b]	124.7	125
$CH=CH-CH_2$ cis[b]	126.7	125
Dihedrals		
$CH_2-CH=CH-CH_2$ trans	180	180
$CH_2-CH=CH-CH_2$ cis	0	0
α (t,cis,s$^\pm$)	180, 0, ±115	180, 0, ±120
β (t,g$^\pm$)	180, ±60	180, ±60

[a] Number in parentheses is the preexponential weighting factor. [b] Indicates conformation of the double bond.

trans-1,4-polybutadiene, and a random copolymer of cis and trans units. The characteristic ratio is given by

$$C_n = \frac{\langle R^2 \rangle}{nl^2} \tag{1}$$

and its temperature dependence by

$$\Delta_T = 1000\frac{d \ln\langle R^2 \rangle}{dT} \tag{2}$$

Here, $\langle R^2 \rangle$ is the mean-square end-to-end distance of the polymer, and nl^2 represents the sum of the squared bond lengths over all backbone bonds of the chain. Calculations were performed for chains of 1000 repeat units. These values, along with experimental estimates, are given in Table 6.

TABLE 6: Characteristic Ratio for 1,4-Polybutadienes from RIS Model Predictions and Experiment

sensitivities[a] source	C_n (323 K)	Δ_T (K^{-1})	Δ_s	Δ_g
cis-1,4-Polybutadiene				
RIS	4.65	+0.29		
RIS modified	4.71	+0.27	0.155	0.009
Flory et al.[b]	5.08	+0.16		
exptl[b]	4.9 (±0.2)	+0.4		
trans-1,4-Polybutadiene				
RIS	5.24	−0.52		
RIS modified	5.65	−0.69	0.0521	0.010
Flory et al.[b]	6.20	−0.11		
exptl[c]	5.8 (±0.2)	−0.65		
Poly($cis_{0.4}$-*r*-$trans_{0.6}$-butadiene)				
RIS modified[d]	5.2			
Flory et al.[b]	5.4			
exptl[e]	5.6			

[a] Sensitivity of the characteristic ratio to changes in temperature, the skew dihedral angle, and the gauche dihedral angle (see text). [b] Ref 34. [c] Ref 37. [d] At 298 K. [e] For a 50/40/10 trans/cis/vinyl copolymer at 298 K, ref 38.

Comparison of RIS predictions with experiment in Table 6 indicates reasonable to good agreement for C_n and its temperature dependence. No adjustments have been made to the energy or geometry parameters obtained from quantum chemistry. For the *trans*-1,4-polybutadiene, a third-order model that allows for more accurate representation of the cisg$^\pm$cis conformers results in a 1% reduction in the characteristic ratio and almost no effect on the temperature dependence thereof. Therefore, we will not further consider the third-order model.

The RIS prediction for C_n of *trans*-1,4-polybutadiene is somewhat lower than the experimental value determined from corrected good solvent measurements.[37] The dimensions of *trans*-1,4-polybutadiene are most sensitive to E_σ, while those of *cis*-1,4-polybutadiene are most sensitive to the value of E_T. Therefore, it should be possible to improve agreement with experiment for *trans*-1,4-polybutadiene by modifying E_σ. This change will have little influence on the characteristic ratio of *cis*-1,4-polybutadiene, where good agreement with experiment is already found. The agreement between RIS predictions and experiment for the characteristic ratio of 1,4-*trans*-polybutadiene and its temperature dependence can be improved if we make $E_\sigma = 0.2$ kcal/mol, an increase of only 0.1 kcal/mol above the quantum chemistry based energy. From our experience with *n*-alkanes, we can estimate that the uncertainty in the conformer energies from quantum chemistry calculations at the level of theory employed in this study for the chemically similar alkenes is around ±0.2 kcal/mol. The RIS predictions with the increased value of E_σ are given in Table 6 as the modified RIS model. As expected, this change has little influence on the predictions for *cis*-1,4-polybutadiene.

The RIS chain dimensions are particularly sensitive to the value used for the skew dihedral angles ϕ_s of the α bonds. As shown in Table 6 ($\Delta_s = dC_n/d\phi_s$), an increase of 1° in this angle results in a 3% increase in the C_n for the *cis*-1,4-polybutadiene and a 1% increase for C_n in *trans*-1,4-polybutadiene. Chain dimensions are relatively insensitive to the value for the gauche dihedral angles ($\Delta_g = dC_n/d\phi_g$) for the β bonds. The temperature dependence of the chain dimensions is insensitive to changes in the geometry parameters. In examining the conformational geometries given in Table 1, it is clear that there is strong coupling between the value of the skew dihedral angle

TABLE 7: RIS Bond Populations in Polybutadienes

	population (323 K)	
sequence[a]	this work[b]	Flory et al.[34]
	cis-1,4-Polybutadiene	
sgs[c]	0.51	0.61
sts	0.35	0.30
sgt	0.08	0.06
stt	0.05	0.03
	trans-1,4-Polybutadiene	
sgs	0.44	0.53
sts	0.30	0.26
cists	0.14	0.17
cisgs	0.09	0.02
cistcis	0.02	0.03

[a] Includes all $\alpha\beta\alpha$ sequences with populations greater than 1%. [b] Using the modified RIS model. [c] Includes all like sequences, e.g., $s^+g^+s^+$, $s^+g^-s^-$.

and the conformation of neighboring bonds. Because of the sensitivity of the predicted characteristic ratio to the skew dihedral angle, this coupling, a feature that is not reproduced in the RIS model, increases the uncertainty in the model predictions of the chain dimensions.

We also compared RIS predictions with experimental data from SANS measurements on melts of a random 50/40/10 trans/cis/vinyl copolymer.[38] We have not parametrized a model for the vinyl units, so we treat these as trans units in our calculations. Because there is no coupling of conformations across the double bonds, as demonstrated by our quantum chemistry calculations on 3-hexene, it is a simple matter to apply the RIS models to random copolymers of trans and cis units.[34] The additional statistical weight matrices for the cis−trans and trans-cis dyads are given in Table 4. Our (modified) RIS model predicts a characteristic ratio somewhat smaller than that seen in the SANS experiments. The difference however is on the order of 10%, which, given the unknown influence of the 10% vinyl units and the sensitivity of the characteristic ratio to the skew dihedral angles, reflects reasonable agreement.

Before proceeding to the force field parametrization, we compare our quantum chemistry based values for the RIS energies, geometries, and conformer populations with those of the empirical model of Flory et al.[34] This model is in most respects similar to the earlier models of Mark.[33,37] In Table 5, the RIS energy and geometry parameters can be compared, while in Table 6 the RIS predictions for chain dimensions and their temperature dependence are shown. Finally, in Table 7, the probabilities of the different intradyad $\alpha\beta\alpha$ sequences are presented.

Comparing the RIS energy parameters, we find that our values are quite similar to those of Flory et al.[34] except for E_T and E_ψ. For the former, the different preexponential factors employed result in similar statistical weights for the α trans state. The difference for the latter energy is discussed below. For the geometry parameters, the important difference is for the skew dihedral angles. Flory et al.[34] used “standard” values of ±120°. Quantum chemistry calculations support values of around ±115° (see Table 1). We can therefore expect the model of Flory et al.[34] to yield 5%/15% larger characteristic ratios than our model for *trans*/*cis*-1,4-polybutadiene when conformer populations are comparable.

Comparing the bond populations for *cis*-1,4-polybutadiene as given in Table 7, both models predict that an appreciable population of the α bonds will be in the trans state. This is required if the RIS predictions of the characteristic ratio and its temperature dependence are to agree with experiment.[33] From Table 6, it can be seen that the predicted characteristic ratio for *cis*-1,4-polybutadiene using our model is somewhat less than that for the model of Flory et al.,[34] despite the higher fraction of α dihedrals in the trans state predicted by our model. This difference can be attributed completely to the difference in the skew dihedral angle, as discussed above. Because of the higher value of E_T, our model predicts a slightly greater temperature dependence of the characteristic ratio for *cis*-1,4-polybutadiene, in better agreement with experiment.

For *trans*-1,4-polybutadiene, our model predicts a somewhat higher cis population for the α bond than the model of Flory et al.[34] despite our higher value of $E_{\chi T}$, due to the very strong second-order coupling in ($\beta\alpha$) $g^\pm$cis conformers in the latter model. Unlike the other parameters employed in the model of Flory et al.,[34] their high value of E_ψ leads to conformer energies for 1,5-hexadiene compounds that are well outside of the uncertainties in the quantum chemistry energies. The combined higher cis population of the α bond and smaller skew dihedral angles in our model yield a lower value for the characteristic ratio of *trans*-1,4-polybutadiene than the model of Flory et al.[34] Our lower value for the ($\beta\alpha$) $g^\pm$cis second-order coupling energy E_ψ allows an appreciable increase in the population of these conformations with increasing temperature, resulting in a fairly large negative temperature dependence of the characteristic ratio, in much better agreement with experiment than that obtained from the model of Flory et al.[34]

Force Field Parametrization

We have parametrized a united atom force field for use in molecular dynamics simulations of bulk 1,4-polybutadiene. The primary advantage of united atom force fields over explicit atom force fields that include hydrogen atoms is readily apparent: an approximate order of magnitude reduction in the computational effort required to generate a trajectory of a given length. Because of our intention to simulate bulk polybutadiene over a wide temperature range for several microstructures, such computational considerations are paramount.

The question remains as to whether a united atom model can accurately represent conformational energetics and intermolecular interactions that fundamentally determine the static and dynamic properties of a polymer melt. In previous work, we have clearly demonstrated the ability of a united atom force field for polyethylene to accurately reproduce a wide variety of static and dynamic properties of this polymer.[15−17] On the other hand, we have shown that for poly(ethylene oxide)[14] an all atom model is required in order to reproduce the conformations of the polymer and important short-range intermolecular interactions. The primary difference in these systems lies in the fact that important specific nonbonded, primarily electrostatic, interactions in poly(ethylene oxide) between hydrogen atoms and oxygen atoms strongly influence the structure and the conformational energies. Such is not the case in polyethylene. Hydrocarbons, such as polyethylene or 1,4-polybutadiene, are essentially nonpolar; therefore, we do not expect important, specific intermolecular interactions to be manifest in either polymer which would be subsequently lost in a united atom representation, nor have we seen evidence of this in the case of polyethylene. However, from the RIS analysis given above it is clear that second-order, or intramolecular nonbonded, effects are manifest in important conformations of polybutadiene. This is in contrast to polyethylene, where the only second-order effect of consequence involves the high-energy g^+g^- sequences. The fact that the polyethylene united atom model we employed does a relatively poor job in reproducing this effect

TABLE 8: Force Field Parameters for 1,4-Polybutadiene

stretch, $E = (1/2)k(r - r^o)^2$	k (kcal/(mol Å^2))	r^o (Å)
CH_2-CH_2	constrained	1.53
$CH-CH$	constrained	1.34
CH_2-CH	constrained	1.50

bend, $E = (1/2)k(\theta - \theta^o)^2$	k (kcal/mol)	θ^o (rad)
CH_2-CH_2-CH	115	1.9487
$CH_2-CH-CH$	89.4	2.1973

torsion, $E = (1/2)\sum k_n(1 - \cos n\phi)$	k_1	k_2	k_3	k_4	k_5	k_6
$CH_2-CH-CH-CH_2$		24.2				
α (cis)	1.033	−0.472	0.554	0.263	0.346	0.164
α (trans)	−0.240	−0.730	1.978	0.082	0.091	−0.056
β	−0.888	−0.619	−3.639	−0.066	−0.247	−0.190

nonbonded, $E = \epsilon\,[(r_{min}/r)^{12} - 2(r_{min}/r)^6]$	ϵ (kcal/mol)	r_{min} (Å)
CH_2-CH_2	0.0936	4.500
$CH-CH$	0.1000	3.800
CH_2-CH	0.1015	4.257

has no important consequences on static or dynamic properties because of the low population of the conformers affected. The same serendipity does not hold for 1,4-polybutadiene, and our united atom model must accurately reproduce the second-order effects given by E_ψ in the RIS representation.

Bonded Parameters

We employed constrained bond lengths and harmonic valence angle bending functions to describe two- and three-center bonded interactions. The force constants and geometry parameters for these functions are given in Table 8. The force constants were taken from the force field of Gee and Boyd.[18] The geometry parameters were chosen so that the equilibrium bond lengths and bond angles of the model compounds best reproduced the values obtained from the quantum chemistry calculations.

Bonded four-center interactions, or torsions, were represented by a six-term cosine series (see Table 8). For the double bond, we initially employed parameters taken from the united atom force field of Gee and Boyd.[18] However, the barrier for rotation of 14.0 kcal/mol yielded by this model is insufficient to preclude cis/trans isomerization at higher melt temperatures. Therefore, we performed SCF/6-311G**//SCF/6-311G** level calculations on 2-butene to obtain a reasonable estimate of the energy of rotation about the double bond. The resulting energies, and fit of a 2-fold cosine function, are shown in Figure 5. The barrier of 24.2 kcal/mol is sufficient to preclude cis/trans isomerization, and the function describes the shape of the torsional wells reasonably well up to quite high energies.

The torsional potentials for the α and β dihedral were parametrized so as to best reproduce the conformational energies of *cis*-2-pentene, *trans*-2-pentene, and 1,5-hexadiene as obtained from quantum chemistry, as illustrated in Figures 2−4. The conformational energies are a function of the bond stretching, bond bending, and nonbonded potentials, in addition to the torsional potentials. The bending potentials and double-bond torsional potentials as given in Table 8 were employed. As we consider intramolecular nonbonded interactions only between centers separated by four or more bonds, the only nonbonded interaction involved in the 2-pentene compounds is that between the end methyl groups. In a polymer, these will be methylene groups and are represented as such in our united atom model for 2-pentene. The CH_2-CH_2 nonbonded potential given in Table 8 is taken from our model for polyethylene.[17] Using a standard nonlinear least-squares procedure, we determined the α bond torsional potential which best reproduced the energies and stationary point geometries for the conformations of 2-pentene as determined from quantum chemistry. The resulting torsional parameters are given in Table 8. Agreement between the force field and quantum chemistry is excellent, as illustrated in Figures 2 and 3. Also shown in Figures 2 and 3 are the conformational energies of 2-pentene yielded by the force fields used in previous simulations of 1,4-polybutadiene. While qualitatively in agreement with the quantum chemistry results, these force fields show important quantitative variations between themselves and are in quite poor agreement quantitatively with quantum chemistry. These discrepancies clearly illustrate the need for a new potential for use in simulations of 1,4-polybutadiene if we desire to make quantitative comparisons with experiment.

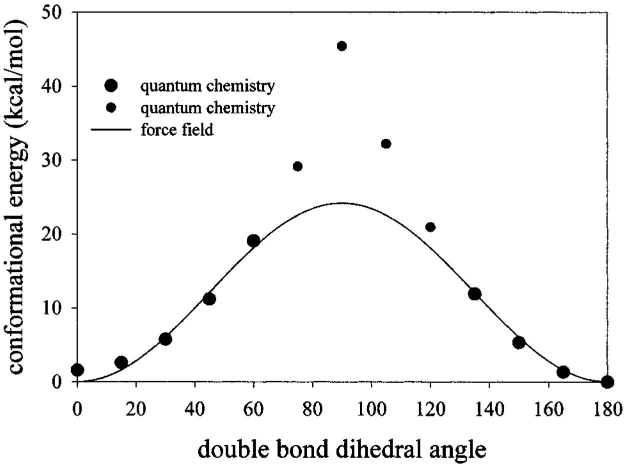


Figure 5. Conformational energy in 2-butene as a function of the double-bond dihedral angle. Only the points given by large circles were used in parametrization of the 2-fold cosine torsional potential.

The energies and geometries of the $s^+\beta s^+$ conformations of 1,5-hexadiene allow us to parametrize the torsional potential for the β bond. While these conformational energies, plotted in Figure 4, do depend upon the $CH-CH$ nonbonded potential, the geometry of these conformations is such that the dependence is fairly weak. As an initial guess we used the CH_2-CH_2 nonbonded potential and then parametrized the β torsional potential to best match quantum chemistry energies and geometries.

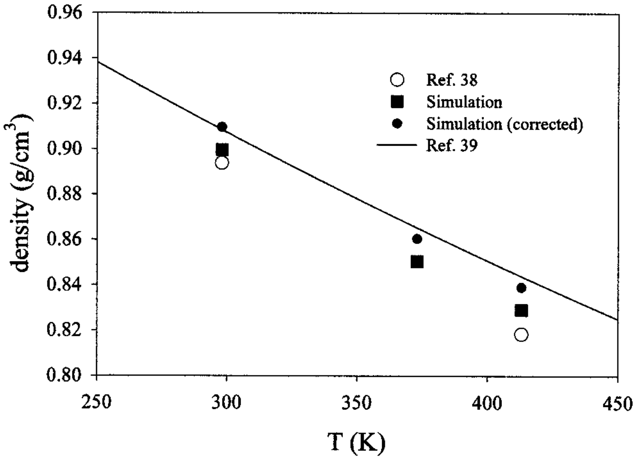


Figure 6. Density of 1,4-polybutadiene as a function of temperature. Simulation (corrected) values include a 1% increase in density over the simulation densities in order to account for molecular weight effects.

As mentioned above, the $(\beta\alpha)$ g$^{\pm}$cis conformations include important second-order effects, represented by E_{ψ} in the RIS model. The ability of our force field to reproduce these effects is reflected in its ability to reproduce the energies of the s^{+}g^{+}cis and s^{+}g^{-}cis conformers of 1,5-hexadiene, which are given in Table 2. In reality interactions in these conformers involve steric interference between hydrogen atoms, and the conformer geometries reflect distortions of the dihedral so as to minimize these interactions. However, by adjusting the CH−CH nonbonded potential, we can do a credible job in reproducing these effects in a united atom representation. The resulting CH−CH nonbonded potential is given in Table 8, as are the torsional parameters for the β bond now determined with this nonbonded potential. Figure 4 shows good agreement between the quantum chemistry and force field conformational energies of s$^{+}\beta$s^{+}. The quantum chemistry and force field energies for all calculated stationary points can be compared in Table 2. For the s^{+}g^{+}cis and s^{+}g^{-}cis conformers, and to a lesser extent the s^{+}g^{+}s^{+} and s^{+}g^{-}s^{+} conformers, the force field energies are somewhat higher than those yielded by quantum chemistry. However, the difference is within the uncertainties in the quantum chemistry energies and in the direction of the modifications made in the RIS model, where the energy of the β gauche states was raised by 0.1 kcal/mol to improve agreement of the characteristic ratio of *trans*-1,4-polybutadiene and its temperature dependence with experiment. Finally, we find that the energy of the 1,5-hexadiene cisgcis conformer is significantly greater than that from quantum chemistry. In fact, it is comparable to that predicted by the second-order RIS model in Table 3. As discussed previously, this conformer has little influence on chain dimensions.

Finally, we parametrized the CH_2−CH nonbonded potential so as to reproduce the density of a melt of 1,4-polybutadiene as a function of temperature. For this purpose, molecular dynamics simulations were performed on a melt of poly(cis$_{0.5}$-*r*-*trans*$_{0.5}$-butadiene). The melt contained 40 such chains of 25 repeat units, generated randomly using Markovian statistics. We performed NPT molecular dynamics simulations on the system at 298, 373, and 413 K. The system was initially equilibrated for 1 ns. Equilibration runs of 200 ps and sampling runs of 400 ps were performed for each change in the nonbonded parameters. Runs of 1 ns were performed for the final parameters, corresponding to the results shown in Figure 6. Additional details on the molecular dynamics simulations will be published elsewhere. Experimental[38,39] and simulation densities are shown in Figure 6 as a function of temperature. The simulation values are in good agreement with those obtained for the 50/40/10 trans/cis/vinyl random copolymer from SANS measurements.[38] If a 1% increase is made to values obtained from simulations in order to account for the low molecular weight of the simulation chains (based on the molecular weight dependence of density for *n*-alkanes and poly(ethylene)), the values are in good agreement with experimental measurements for *cis*-1,4-polybutadiene.[39] The thermal expansion coefficient from simulation for the random copolymer appears to be slightly larger than the experimental value for *cis*-1,4-polybutadiene[39] given by the temperature dependence of the solid line in Figure 6.

Finally, on the basis of our experiences in parametrizing the torsional potential for the allyl bond in *cis*-2-pentene and *trans*-2-pentene, a comment on the transferability of the force field is in order. Previous efforts to parametrize force fields for the allyl bond based on quantum chemistry calculations have employed relatively low level quantum chemistry calculations on 1-butene.[26,27] For these force fields, and for those employed previously in simulations of polybutadiene,[19,22] the same torsional potential is employed for allyl bonds adjacent to cis double bonds as is used to describe allyl bonds adjacent to trans double bonds. Our quantum chemistry calculations show that the energies of the s$^{\pm}$tcis conformer of 1,5-hexadiene and the cis conformer of 1-butene are nearly the same as that for the cis conformer of *trans*-2-pentene, indicating that the former two molecules are reasonable model compounds for the allyl bond adjacent to a trans double bond. However, examination of Table 8 indicates that the parametrized torsional potential for the allyl bond in *cis*-2-pentene is significantly different from that for *trans*-2-pentene. Hence, for the united atom model, a torsional potential parametrized for an allyl bond based on *trans*-2-pentene (or 1-butene) *cannot* be used to describe an allyl bond adjacent to a cis double bond. In parametrization of an explicit atom force field for these model compounds, we find that the same effects are manifest. Hence, our conclusion is that the torsional characteristics of the allyl bond are fundamentally different depending on whether the adjacent double bond is trans or cis. This difference cannot be represented simply through differences in the intramolecular nonbonded interactions, as is assumed implicitly in the other force fields discussed here.

Acknowledgment. G.S. gratefully acknowledges support of Sonderforschungsbereich 262 during his stay in Mainz.

References and Notes

(1) Morton, M.; Fetters, L. J. *Rubber Rev.* **1975**, *48*, 359.

(2) Deegan, R. D.; Nagel, S. R. *Phys. Rev. B* **1995**, *52*, 5653.

(3) Arbe, A.; Richter, D.; Colmenero, J.; Farago, B. *Phys. Rev. E* **1996**, *54*, 3853.

(4) Guillermo, A.; Dupeyre, R.; Cohen-Addad, J. P. *Macromolecules* **1990**, *23*, 1291.

(5) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122.

(6) Richter, D.; Frick, B.; Farago, B. *Phys. Rev. Lett.* **1988**, *61*, 2465.

(7) Frick, B.; Richter, D.; Ritter, Cl. *Europhys. Lett.* **1989**, *9*, 557.

(8) Frick, B.; Farago, B.; Richter, D. *Phys. Rev. Lett.* **1990**, *64*, 2921.

(9) Kanaya, T.; Kaji, K.; Inoue, K. *Macromolecules* **1991**, *24*, 1826.

(10) Zorn, R.; Richter, D.; Frick, B.; Farago, B. *Physica A* **1993**, *201*, 52.

(11) Arbe, A.; Buchenau, U.; Willner, L.; Richter, D.; Farago, B.; Colmenero, J. *Phys. Rev. Lett.* **1996**, *76*, 1872.

(12) Zorn, R.; Kanaya, T.; Kawaguchi, T.; Richter, D.; Kaji, K. *J. Chem. Phys.* **1996**, *105*, 1189.

(13) Smith, G. D.; Yoon, D. Y.; Zhu W.; Ediger, M. D. *Macromolecules* **1994**, *27*, 5563.

(14) Smith, G. D.; Yoon, D. Y.; Wade, C. G.; O'Leary, D.; Chen, A.; Jaffe, R. L. *J. Chem. Phys.* **1997**, *106*, 3798.

(15) Smith, G. D., Paul, W.; Yoon, D. Y.; Zirkel, A.; Hendricks, J.; Richter, D.; Schober, H. *J. Chem. Phys.* **1997**, *107*, 4751.

(16) Paul, W.; Smith G.; Yoon, D. Y.; Farago, B.; Rathgaber, S.; Zirkel, A.; Willner, L.; Richter, D. *Phys. Rev. Lett.*, in press.

(17) Paul, W.; Yoon D. Y.; Smith, G. D. *J. Chem. Phys.* **1995**, *103*, 1702.

(18) Han, J.; Gee, R. H.; Boyd, R. H. *Macromolecules* **1994**, *27*, 7781.

(19) Gee, R. H.; Boyd, R. H. *J. Chem. Phys.*.**1994**, *101*, 8028.

(20) Gee, R. H.; Boyd, R. H. *Polymer* **1995**, *36*, 1435.

(21) .Li, Y.; Mattice, W. L. *Macromolecules* **1992**, *25*, 4942.

(22) Kim, E.; Misra, S.; Mattice, W. L. *Macromolecules* **1993**, *26*, 3424.

(23) Kim, E.; Mattice, W. L. *J. Chem. Phys*. **1994**, *101*, 6242.

(24) Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035.

(25) .Wiberg, K. B.; Schreiber, S. L. *J. Org. Chem.* **1988**, *53*, 783.

(26) Petterson, I.; Gundertofte, K. *J. Comput. Chem*. **1991**, *12*, 839.

(27) Broeker, J. L.; Hoffman, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006.

(28) Smith, G. D.; Jaffe, R. L. *J. Phys. Chem.* **1996**, *100*, 18718.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.1* Gaussian, Inc.: Pittsburgh, PA, 1995.

(30) Tosi, C.; Ciampelli, F. *Eur. Polym. J.* **1969**, *5*, 759.

(31) Kondo, S.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 471.

(32) Durig, J. R.; Compton, D. A. C. *J. Phys. Chem*. **1980**, *84*, 773.

(33) Mark, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4354.

(34) Abe, Y.; Flory, P. J. *Macromolecules* **1971**, *4*, 219.

(35) Rehahn, M.; Mattice, W. L.; Suter, U. W. *Rotational Isomeric State Models in Macromolecular Systems: Advances in Polymer Science 131/132*; Springer: New York, 1997.

(36) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley and Sons: New York, 1969.

(37) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.

(38) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.

(39) Paul, D. R.; DiBenedetto, A. T. *J. Polym. Sci. C* **1965**, *10*, 17.