Notice that both θ and $\tilde{\theta}$ scale as N^2 but have different dependences on the tensile force. The spectrum is now determined by using scaling arguments analogous to the end of section II. For $\xi_t^{-1} \gg q \gg R_F^{-1}$

$$\Delta\omega_q \approx \tilde{\theta}^{-1}\tilde{F}_2(qR_F) \tag{29}$$

where $\tilde{F}_2(x) \sim 1$ for $x \sim 1$ and $\tilde{F}_2(x) \sim x^p$; $x \gg 1$; the exponent p is determined by the condition $\Delta\omega_q$ and should be independent of the chain length N. This immediately leads to $p = 2/\nu = {}^{10}\!/_3$ and

$$\Delta\omega_q \approx (k_BT/6\pi\eta)q^{10/3}\xi_t^{1/3} \tag{30}$$

which differs from both the ideal q^4 chain dependence and the de Gennes $q^{2+1/\nu}$ behavior for unstretched ($\xi_t \rightarrow \infty$) Rouse chains with excluded volume. For shorter wavelengths, $q \gg \xi_t^{-1}$, we expect to find $\Delta\omega_q$ independent of the screening length; i.e., $F_1(q_t) \sim 1$ for $q\xi_t \sim 1$ and $\tilde{F}_1(q\xi_t) \sim (q\xi_t)^r$ for $q\xi_t \gg 1$ where r is found from the condition that $\Delta\omega_q$ is dependent of ξ_t. This leads to $r = -{}^1\!/_3$ and the usual Zimm q^3 form (eq 4).

IV. Conclusion

In summary, we have shown that for stretched polymers the parameter $\xi_t = (\beta f)^{-1}$ in addition to being the screening length for the excluded volume effects is also the characteristic distance beyond which the hydrodynamic interactions lead to only logarithmic corrections to free draining behavior. Then, using scaling arguments, we found functional dependences for the width of the incoherent inelastic neutron scattering peak. For sufficiently short wavelengths, $q\xi_t \gg 1$, the ideal chain q^3 behavior obtains, characteristic of complete hydrodynamic coupling between the monomers. For $R_F^{-1} \ll q \ll \xi_t^{-1}$, Rouse-like behavior modified by the excluded volume interactions to give $\Delta\omega_q \propto q^{10/3}$ is found. The rather small difference between 3 and ${}^{10}\!/_3$ might be difficult to detect experimentally.

In principle, the quantity $\Delta\omega_q$ may be determined by quasielastic neutron or light scattering. Indeed recently Adam and Delsanti[12] have observed the q^3 law for undeformed coils in light scattering.

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(8) Because the link length a and the hydrodynamic radius of a monomer b are comparable, we shall often neglect the difference and write the equations assuming $a = b$.

(9) This work[2] has been submitted to *Macromolecules* in two parts: (I) deals with the Rouse limit while (II) includes the hydrodynamic interactions.

(10) See, for example, L. Landau and E. Lifshitz, "Fluid Mechanics", Pergamon Press, London, 1959, Chapter 2.

(11) So long as the blob radius ξ_t is large compared to a monomer, the viscous damping rate will generally dominate the microscopic damping rate W.

(12) M. Adam and M. Delsanti, private communication.

Calculation of Phenyl Group Rotation in Polystyrene by Means of Semiempirical Potentials

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ABSTRACT: By means of a set of semiempirical potentials the activation energies of phenyl group rotation in polystyrene have been calculated. The backbones (isotactic and syndiotactic, isotactic with kink) have been given a high degree of flexibility. The activation energies have been determined by consecutive rotation of the rotational angle of the phenyl group between 0° and 180° in steps of 20° and by minimizing the energy with respect to all other variables. The lowest activation energy of 10.3 kcal/mol was found in the isotactic 3/1-helix. For other conformations the activation energies do not exceed ca. 20 kcal/mol. Higher values do not occur because of conformational changes of the flexible backbone.

Recently, Tonelli has summarized the efforts to interpret mechanical relaxation processes in polystyrene.[1] By means of semiempirical atomistic calculations he investigated the rotation of the phenyl group in syndiotactic polystyrene chain segments. In accordance with Reich and Eisenberg[2] he stated that phenyl group rotation with activation energies of as low as 10 kcal/mol is permitted only if the backbone adopts sterically unfavorable conformations.

In this paper, atomistic calculations with well tested semiempirical potentials, already performed on isotactic polystyrene,[3] have been extended to phenyl group rotation in isotactic as well as in syndiotactic polystyrene. During minimization of the conformational energy the flexibility of the backbone was explicitly taken into account. Due to the high degree of freedom of the chain segment considered we got new detailed results concerning phenyl group rotation and its coupling to the backbone.

Method of Calculation

The conformational energy and its gradient have been calculated by an effective matrix algorithm which allows a fast computation with minimal computer core storage.[6] In order to determine minima of the energy, the algorithm of Fletcher and Powell[7] has been used.

The representative chain segment containing the phenyl group to be rotated consists of flexible repeating units (ru) and of adjacent ru at both sides of the variable region, which are fixed to the ideal structure considered[3,8] (cf. Table I).

All nonbonded (steric) interactions between the atoms have been taken into account, except interactions between the

Table I
Characterization of the Chain Segments

Polystyrene	Isotactic chain	Syndiotactic chain
Repeating unit (ru)	$-CH_2-CH(C_6H_5)-$	$-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-$
No. of flexible ru	8	4
No. of variables per ru	13	26
No. of adjacent rigid ru (at each side)	4	2

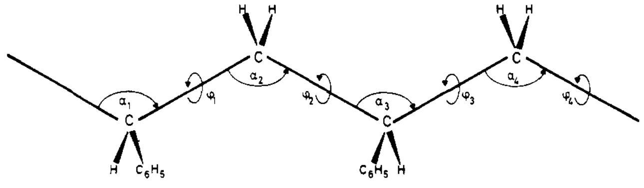

Figure 1. Definition of the dihedral and valence angles used in Table II (φ_i = 0°, describing a planar conformation).

atoms of the rigid chain ends.[10] The rotational angle of the phenyl group to be rotated is assigned to values between 0° and 180° in steps of 20°.

The set of potentials used in this paper has already been used to calculate ideal and defective structures of several polyolefins.[4,5,9] Recent calculations using these potentials have shown that they are also applicable to the isotactic polystyrene chain and to the ideal benzene crystal.[3]

Results and Discussion

(1) Phenyl Group Rotation in Syndiotactic Polystyrene. In addition to the investigation of ideal structures of the isotactic polystyrene chain[3] several syndiotactic ideal structures have been calculated. A brief characterization of the conformations is given in Table II (conformation energy differences are given with respect to the energy of two ru of the isotactic 3/1-helix).

In order to calculate activation energies of the phenyl group rotation, the tttt sequence (the energetically most favored conformation) and the gggg sequence are selected.

The activation energies obtained by minimizing the conformational energy with respect to the variables adjacent to the rotated phenyl group are:

tttt sequence: ΔH = 11.7 kcal/mol

gggg sequence: ΔH = 19.7 kcal/mol

These results are not in accordance with calculations performed by Tonelli.[1] He found that only in the case of the sequences tḡgt, gḡgt, or ḡḡgt are the activation energies ca. 9.5 kcal/mol, while other sequences (e.g., the tttt sequence) lead to activation energies higher than 100 kcal/mol. Our calculations, however, show that in sequences with high thermodynamic probability the activation energies do not exceed 20 kcal/mol.

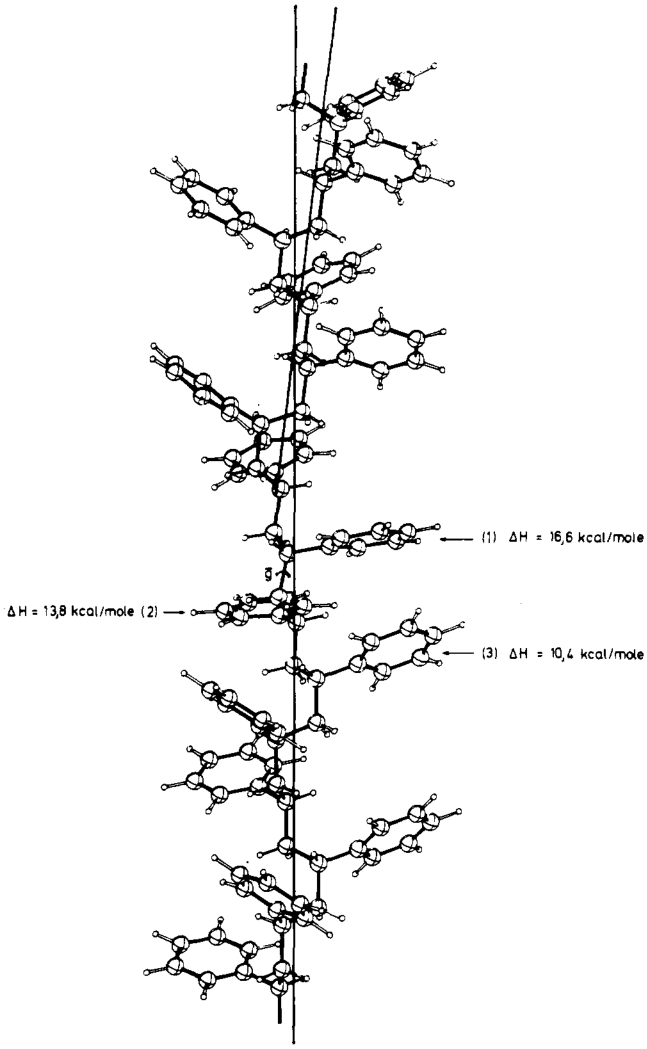

Figure 2. Activation energies of phenyl group rotation near a ḡ kink in isotactic polystyrene.

These discrepancies are probably caused by two facts: (a) The sets of potentials used differ considerably. In order to test the accuracy of the potentials used by Tonelli,[1] we tried to calculate the structure and cohesion energy of the ideal benzene crystal. Contrary to the results obtained with our potentials, the agreement with experimental data was found to be poor. (Cohesion energy >0 in the range of experimentally known lattice parameters!) We feel that the repulsive terms

Table II
Conformations of the Syndiotactic Polystyrene Chain

Conformation (approx)		Dihedral angles				Valence angles				ΔE per ru, kcal/mol
		φ_1	φ_2	φ_3	φ_4	α_1	α_2	α_3	α_4	
4*52/1	tttt	−1.16	−1.20	1.20	1.16	114.04	110.81	114.04	110.42	−1.57
4*2/1	ḡḡtt	−108.12	−108.44	−0.60	−0.84	114.54	112.22	113.86	111.90	0.18
4*4/1	ḡttt	−88.78	−6.24	0.62	−2.38	114.22	110.92	114.07	112.49	0.79
4*11/1	ḡḡtḡ	−111.46	100.71	9.37	−117.23	114.32	111.60	116.47	112.74	2.56
4*28/1	tḡtg	−9.92	−90.77	11.95	89.54	113.50	112.67	113.50	112.27	2.77
4*18/1	gggg	125.84	126.43	113.83	113.36	120.33	114.65	114.76	113.85	3.96
4*3/1	ḡtḡt	−114.33	−28.79	−119.37	7.04	115.13	111.92	116.78	113.30	5.13

of his potentials are too high. (b) The approximations used by Tonelli suppress the flexibility of the backbone. That means that during rotation of the phenyl group neither valence angles nor dihedral angles are allowed to change. These facts may cause the extremely high reported activation energies.

In addition, we recalculated the three sequences reported by Tonelli and found no energy minimum in the range of these conformations. That means that for these conformations activation energies do not exist.

The apparent stability of Tonelli's conformations is forced by the rigid backbone (cf. *b*) and disappears for a nonrigid backbone with interactions between the atoms.

(2) Phenyl Group Rotation in Isotactic Polystyrene. The investigations of the mobility of the phenyl group have been extended to isotactic polystyrene.

(a) Rotation in Ideal Backbones. Starting with the isotactic structures already determined,[3] the activation energies have been calculated in the same way as for syndiotactic polystyrene. The following results have been obtained:

$$\text{gt sequence: } \Delta H = 10.3 \text{ kcal/mol}$$

$$\text{tt sequence: } \Delta H > 30 \text{ kcal/mol}$$

$$\text{gg sequence: } \Delta H = 13.7 \text{ kcal/mol}$$

In the case of the tt sequence, the value $\Delta H > 30$ kcal/mol is caused by strong phenyl–phenyl interactions and is obtained only under the restriction that the tt conformation of the backbone is preserved. Without restrictions, the tt conformation is destroyed in the neighborhood of the rotating phenyl group (two adjacent dihedral angles change from t to g), and so the activation energy is decreased to ca. 17 kcal/mol, and the energy difference between the two minima is increased from 0 to 7.5 kcal/mol.

(b) Rotation in Backbones with Defects (Kinks). Using already determined conformations of two kinks in the isotactic polystyrene chain,[3] the activation energies of phenyl groups near the defects have been investigated. The results for a $\bar{g}$ kink are given in Figure 2.

The corresponding values for a t kink (the same C–C bond rotated from g to t instead of from g to $\bar{g}$) are: (1) kink is annihilated, (2) $\Delta H = 12.2$ kcal/mol, and (3) kink is annihilated. In cases (1) and (3) the strong coupling between the phenyl group and the backbone causes an annihilation of the kink, as the activation energy (rotation in the backbone) $\Delta H_{\mathrm{t}\rightarrow\mathrm{g}}$ is smaller than $\Delta H_{\bar{\mathrm{g}}\rightarrow\mathrm{g}}$.[3]

We expected that the phenyl group rotation would be favored near defects, as there is no regular steric arrangement of the side groups, which were assumed to restrict the rotation to a higher degree.

The results given in Figure 2, however, show the opposite behavior; the activation energies increase in the neighborhood of the defect.

The calculations reported above may be summarized as follows: Activation energies of phenyl group rotation are in the range between ca. 10 and 20 kcal/mol, if the backbone is flexible. For low activation energies the phenyl–backbone interaction dominates, while for increasing activation energies the phenyl–phenyl interaction becomes more important.

As these values of activation energies are found in probable chain segments, energetic considerations cannot rule out phenyl group rotation as a mechanism for mechanically activated relaxation processes.[11]

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(10) For simplicity the phenyl ring was taken rigid and therefore interactions within the ring have also been omitted.
(11) Note added in proof: A recent carbon-13 NMR study of molecular motion of polystyrene in solution by Y. Inoue and T. Konno (*Polym. J.*, **8(5)**, 457 (1976)) reports 10.5 and 13.6 kcal/mol for the activation energies of phenyl ring rotation in isotactic and syndiotactic polystyrene, respectively. These experimental data confirm our calculations. A detailed discussion will be given elsewhere.

Notes

Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. 3. Oligo(isobutylene terephthalate)'s Having Pendant ω-Carbazolylalkyl Groups

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In the preceding articles, we have discussed the specificities of molecular interactions in polymeric systems in comparison with the monomeric model systems.[1–4] It was shown that the interactions between the polymer side chains depend on the distance between side chains if the side chain structures are identical.[4] The solvent effects on exciplex formation between carbazolyl and terephthalate groups, both bound to a polymer, were found to be different from those observed in the corresponding monomer model systems, which were attributed to the specific solvation of polymer chains.[3] This exciplex formation should also be affected by the structure of side chains at least in two ways. First, the encounter probability of the excited carbazolyl groups on the side chain forming an exciplex with the ground state terephthalate groups on the main chain should be a function of the structure of the side chain. Second, the solvation of polymer chains should be influenced by the structure of the side chain.

This note describes the side chain effects on exciplex formation of a pendant carbazolyl group with a terephthalate group in the main chain of an oligoester.