On cooling, a dark brown product precipitated which was filtered and dried to yield 14 g (75%) of crude **4**. Purification was carried out by sublimation at 240° (10^{-2} mm) and subsequent recrystallization from 1,2,4-trichlorobenzene to yield 2.2 g (11%) of **4**, mp 310–312°.

Poly(*p*-phenylene) (6). Polymerization Procedure. Equimolar amounts of the 5,5′-*p*-phenylenebis-2-pyrone (**4**) and *p*-diethynylbenzene were weighed into a glass ampoule along with enough solvent (1,2,4-trichlorobenzene, α-chloronaphthylene, or 1,2-dichloroethane) to obtain a solution about 1.5 wt % in total monomer. (Typically, 1 mmol of each monomer in 30 ml of solvent was employed.) The reaction mixture was then degassed on a vacuum line by three freeze(−198°)–evacuate–thaw cycles, and the ampoule was sealed *in vacuo*. The ampoule was placed in a 500-ml Parr bomb with 100 ml of the reaction solvent, and the bomb was sealed and heated to the desired temperature for the desired reaction time (Table I). The bomb was then cooled and opened; the polymer in each case had precipitated. The contents of the ampoule were poured into methanol and the resulting precipitate was filtered. The polymers were dried under reduced pressure at 80° for 24 hr: ir 800 cm^{-1} (CH def, 2 adj H); λ_{max}(refl) 340 nm.

Anal. Calcd for $C_{79}H_{52}O_2$ (**6**, $n = 2$): C, 91.59. Found: C, 91.11, 91.20 (two different samples).

Sulfonation of Poly(*p*-phenylene).[22] To 30 ml of concentrated sulfuric acid heated to 250° under a constant stream of nitrogen was added 0.2 g of the poly(*p*-phenylene) sample to be sulfonated. The mixture was stirred under these conditions for 120 hr. The black reaction mixture was then cooled and poured into ice–water, and the polymer was separated by centrifugation. The polymer was washed with water several times and dried under reduced pressure: ir 1150 and 1015 (sulfonic acid), 875 (CH def, isolated), 815 cm^{-1} (CH def, 2 adj H).

Anal. Calcd for 92% $(C_6H_4SO_3)_n$, 8% $(C_6H_4)_n$: C, 50.0. Found: C, 50.2.

Acknowledgment. This research was supported in part by the U. S. Army Research Office, Durham, N. C. The authors wish to acknowledge the assistance of Mr. L. Stoel in obtaining the reflectance spectra, Dr. N. C. Baenziger for the X-ray data, Mr. L. Mathias for the tga, and Mr. G. K. Noren for assistance.

Calculations on the Unperturbed Dimensions of Polypropylenes

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ABSTRACT: Using the matrix method of Flory the unperturbed dimensions $\langle r_0^2 \rangle / nl^2$ and their temperature coefficients have been evaluated as function of tacticity for polypropylene. The model parameters have been varied systematically within reasonable limits to fit the experimental results. The minimum positions of the rotational bond angles probably do not deviate more than 5° from planar trans and from symetrically staggered gauche, respectively. Entropy contributions to the free energies of the rotational isomers are discussed with respect to the influence on the temperature coefficient.

For linear polymers the unperturbed dimensions and their temperature coefficients can be evaluated with the rotational isomeric state model.[1] Energies and rotation angles of the prefered conformations can be taken from semiempirical energy calculations.[2,3] Neglecting some details of such calculations, Flory and coworkers[4] have proposed a three-state model, which should describe all vinyl polymers. Therefore, this model seems to be especially suitable for an extension to vinyl copolymers.[5] Such an approach has to be based on parameters of the corresponding homopolymers.

In this paper parameters are reported which describe the experimental data on polypropylenes. These have been found by studying the influences of the variables on the unperturbed dimensions. The exactness of the free energies of the rotational isomeric states, required for a good fit with experiment, may be estimated from the influence of a variation of the corresponding parameter values. Furthermore, entropy contributions to the free energies of the isomeric states are discussed with regard to their influence on the temperature coefficients of the unperturbed dimensions.

Theory

According to Flory, *et al.*,[4] the free energy of a chain conformation is expressed as a sum, where each term is dependent on *one* bond rotational angle only (first-order interactions) or on two consecutive bonds (second-order interactions). The three isomeric states of a bond are shown in Figure 1. A mirror reflection of the diagrams inverts the asymetric center and reverses the sign of the rotation angle, whereas the interaction energy is not altered. Therefore each diagram represents two states of different asymmetric center with a rotation angle of the same absolute value but with opposite sign.

The first-order free energies of the states are taken relative to the gauche (g) state. (In Figure 1 their statistical weights are put in parentheses.) In the trans state, CH_3 instead of CH_2 is syn with respect to CH. Therefore, it is expected that η may be a little lower than unity, partly due to the increased restriction of internal rotation for the methyl group. For $\bar{g}$ CH is syn to CH_3 as well as to CH_2. This corresponds to $\tau < \eta$.

Second-order interactions involve essential steric overlapping of groups separated by four bonds, *i.e.*, CH, CH_2, and CH_3. Calculations on *n*-pentane[2,3] indicate that this overlapping yields two minima, which are separated by a low

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.
(2) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).
(3) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **44**, 3054 (1966).
(4) See ref 1, Chapters III and VI; P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966); P. J. Flory and Y. Fujiwara, *Macromolecules*, **2**, 315 (1969); Y. Fujiwara and P. J. Flory, *ibid.*, **3**, 280 (1970); A. D. Williams and P. J. Flory, *J. Amer. Chem. Soc.*, **91**, 3111 (1969).
(5) U. Biskup and H.-J. Cantow, *Makromol. Chem.*, **148**, 31 (1971).

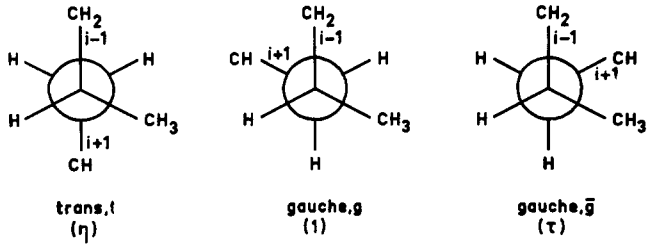

Figure 1. Newman projections of the rotational isomeric states of bond i.

barrier. Since the model of Flory describes these conformations by one isomeric state only, the free energy of this state is expected to include a higher entropy contribution than for the energetically favored states. The statistical weights are ω for a pair of CH_2 or CH groups and ω' for an interaction between CH_2 and CH_3. ω'' refers to CH_3 interacting with CH_3. If CH_3 groups are involved in second-order interactions, an additional restriction to their hindered rotation is effected. Therefore, ω' and ω'' are assumed to be lower than ω. We decided to approximate $\omega' = \omega''$, because it turns out that the influence of ω' as well as of ω'' is much less pronounced than that of ω.

The statistical weight matrices built up from the above parameters are

$$U' = \begin{bmatrix} \eta & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix}$$

$$U_i'' = \begin{bmatrix} \eta\omega'' & 1 & \tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\omega & \omega' & \tau\omega\omega'' \end{bmatrix}$$

$$U_s'' = \begin{bmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega'' & \omega & \tau\omega'^2 \end{bmatrix}$$

U' is assigned to bonds $CHCH_3$–CH_2 and U'' to CH_2–$CHCH_3$. Index i indicates an isotactic and s a syndiotactic dyad. The matrices reduce to the order 2 if conformations with factors of the third columns in the U matrices are neglected.

The supplement θ of the backbone bond angle and the angles φ characterizing the exact positions of the isomeric states have to be specified. We have taken $\theta = 68°$ throughout. For the states of Figure 1 it is assumed

$$\varphi_t = \Delta\varphi \qquad \varphi_g = 120° - \Delta\varphi \qquad \varphi_{\bar{g}} = -120°$$

This scheme holds for all types of bonds if left-in addition to right-handed coordinate systems are used.

For nonstereoregular chains sequences of dyads are generated with random numbers assuming Bernoullian statistics. The characteristic ratios $\langle r_0^2\rangle/nl^2$ of chains (with constant number n of bonds) containing isotactic dyads according to constant probability f_i of the enchainment have been calculated using identical sequences of random numbers. Thus, varying the conformation parameters for chains being identical with respect to the sequence structure, the calculated differences of $\langle r_0^2\rangle/nl^2$ are much more reliable than those computed with chains of constant f_i fluctuating, however, in the actual enchainment.

TABLE I
UNPERTURBED DIMENSIONS OF POLYPROPYLENES FROM VISCOSITY MEASUREMENTS WITH $\Phi = 2.5 \times 10^{21}$

Tacticity	Solvent	Temp, °C	$\langle r_0^2\rangle/nl^2$
Syndiotactic	Toluene[a]	30	6.69
	Heptane[a]	30	6.69
	Isoamyl acetate[a]	45 (θ)	6.71
	Decalin[a]	135	5.18
Atactic	Benzene[b]	30	6.38
	Toluene[b]	30	6.38
	Cyclohexane[b]	30	6.55
	Isoamyl acetate[c]	34 (θ)	6.79
	Chloronaphthalene[c]	74 (θ)	7.17
	Cyclohexanone[c]	92 (θ)	6.90
	Phenyl ether[c]	153 (θ)	5.43
Isotactic	Diphenyl[d]	125.1 (θ)	6.35
	Decalin[c]	135	5.28
	Diphenyl ether[d]	142.8 (θ)	5.93
	Phenyl ether[c]	145 (θ)	5.78
	Dibenzyl ether[d]	183.2 (θ)	5.00

[a] Data of H. Inagaki, T. Miyamoto, and S. Ohta, *J. Phys. Chem.*, **70**, 3420 (1966). [b] Data of F. Danusso and G. Moraglio, *Rend. Accad. Naz. Lincei*, [8] **25**, 509 (1958); *Makromol. Chem.*, **28**, 250 (1958). [c] Data of J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **67**, 1922 (1963). [d] Data of A. Nakajima and A. Saijyo, *J. Polym. Sci., Part A-2*, **6**, 735 (1968).

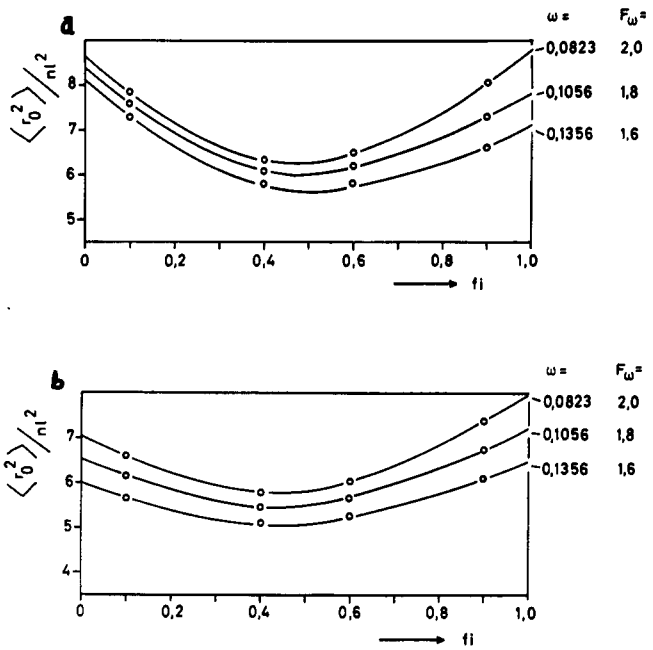

Figure 2. Dependence of the characteristic ratios on ω; 100 monomer units, $\Delta\varphi = 0°$, $\eta = 1$, $\omega' = 0.018$ ($F_{\omega'} = 3.22$ kcal at 130°): (a) 2 × 2 statistical weight matrices; (b) 3 × 3 statistical weight matrices, $\tau = 0.6$ ($F_\tau = 0.41$).

Results and Discussion

To find reasonable parameters for polypropylenes the calculations have to be compared with published experimental results (see Table I). In the following we present the most illustrative data, obtained by a systematic variation of the parameters. The values of $\langle r_0^2\rangle/nl^2$ are averaged for 4 chains with 100 monomer units and refer to a temperature of 130°.

Figure 2a,b shows that calculations with statistical weight matrices of order 2 are useful for estimating the influence of the various parameters on $\langle r_0^2\rangle/nl^2$. The range of ω is sug-

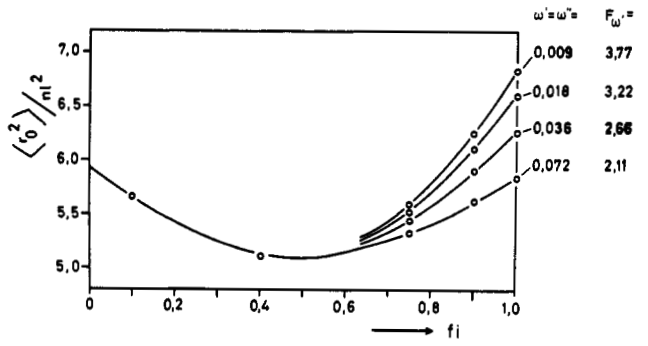

Figure 3. Dependence of the characteristic ratios on ω'; 100 monomer units, $\Delta\varphi = 0°$, $\eta = 1$, $\tau = 0.6$, $\omega = 0.1356$ ($F_\omega = 1.6$).

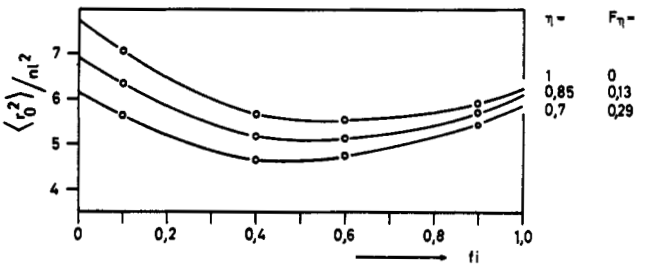

Figure 4. Dependence of the characteristic ratios on η; 100 monomer units, $\Delta\varphi = 5°$, $\omega = 0.0932$ ($F_\omega = 1.9$), $\tau = 0.6$, $\omega' = 0.0565$ ($F_{\omega'} = 2.3$).

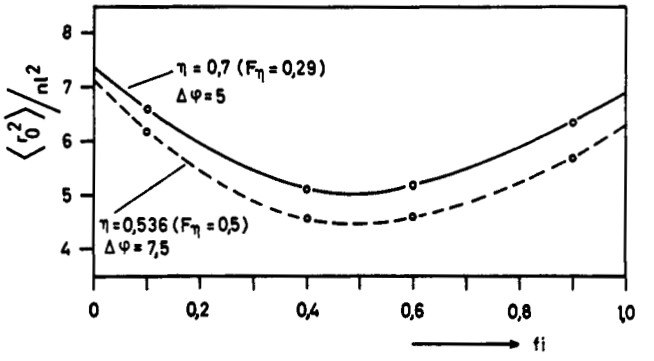

Figure 5. Characteristic ratios for low η values; 100 monomer units, $\tau = 0.4$ ($F_\tau = 0.73$), $\omega = 0.0726$ ($F_\omega = 2.1$), $\omega' = 0.0441$ ($F_{\omega'} = 2.5$).

gested by investigations on polymethylene.[2] As a relatively low value has been assigned to $\omega' = \omega''$ in the calculations of Figure 2, the curves indicate that the free energy F_ω is probably not higher than 2.0 kcal/mol. A variation of ω' and ω'', respectively, has an influence on $\langle r_0^2\rangle/nl^2$ for isotactic configurations only (see Figure 3). The value of $\tau = 0.6$ seems to be somewhat arbitrary. A considerably lower value, however, leads to a more pronounced dependence of $\langle r_0^2\rangle/nl^2$ on the fraction of isotactic dyads f_i (see Figure 2a), which is not compatible with the experimental results, whereas a value a little less than unity is not probable because of the results on model compounds.[6]

On the basis of their potential calculations, Borisova and Birshtein[7] have proposed that the conformational energy of an all-trans chain is reduced if two consecutive bonds flanking

(6) See ref 1, pp 208–210.
(7) N. P. Borisova and T. M. Birshtein, *Vysokomol. Soedin.*, 6, 1234 (1967).

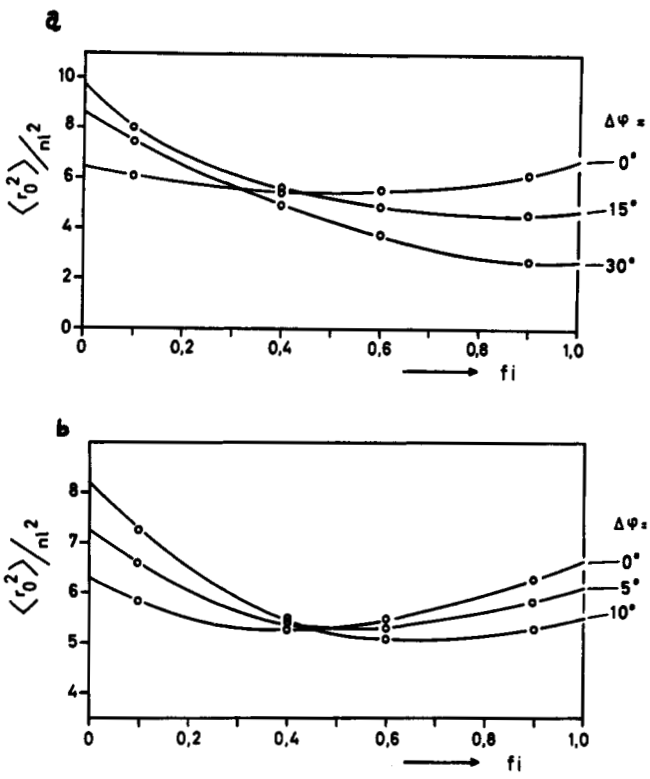

Figure 6. Dependence of the characteristic ratios on $\Delta\varphi$; 100 monomer units, $\tau = 0.6$, $\omega' = 0.0565$ ($F_{\omega'} = 2.3$): (a) $\eta = 1$, $\omega = 0.1056$ ($F_\omega = 1.8$); (b) $\eta = 0.9$ ($F_\eta = 0.09$), $\omega = 0.0932$ ($F_\omega = 1.9$).

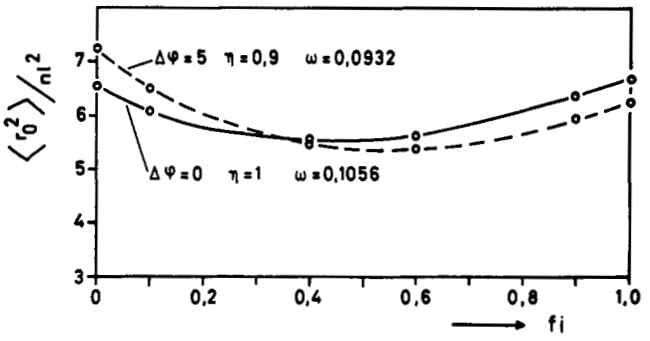

Figure 7. Characteristic ratios to describe the experimental results; 400 monomer units, $\tau = 0.6$, $\omega' = 0.0565$ ($F_{\omega'} = 2.3$).

CH_2 are transformed to the gauche (g) state. In the model of Flory, this is described by $\eta < 1$. From our calculations it can be concluded that η is only slightly lower than unity (see Figure 4), whereas the results of Borisova and Birshtein correspond to $\eta = 0.54$ ($F_\eta = 0.5$ kcal). For configurations of high tacticity, even with relatively low η values, agreement could be obtained with the experimental data for $\langle r_0^2\rangle/nl^2$, if the second-order parameters are assumed to be lower than the values proposed by the results on polymethylene. With this parameter set for atactic configurations ($f_i \approx 0.5$), however, the theoretical values of $\langle r_0^2\rangle/nl^2$ are below the experimental data (see Figure 5).

It has been suggested[4] that the positions of the rotational minima deviate about 10–20° from planar trans and symetrically staggered gauche g due to nonbonded interactions. This is described by $\Delta\varphi$. The curves of Figure 6 show that $\Delta\varphi > 5°$ leads to values of $\langle r_0^2\rangle/nl^2$ which are higher than the experi-

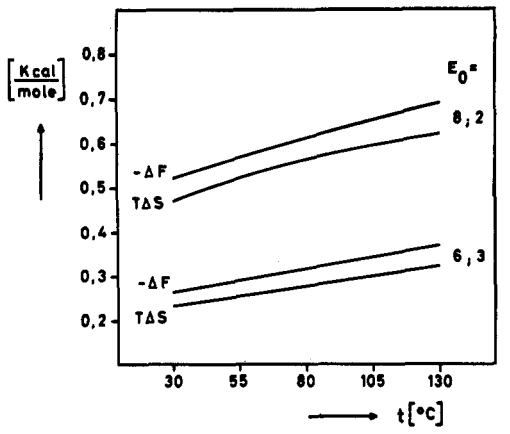

Figure 8. Free energy and entropy differences for potential valleys; $E = {}^1/_2E_0(1 - \cos 3\varphi)$ differing in E_0.

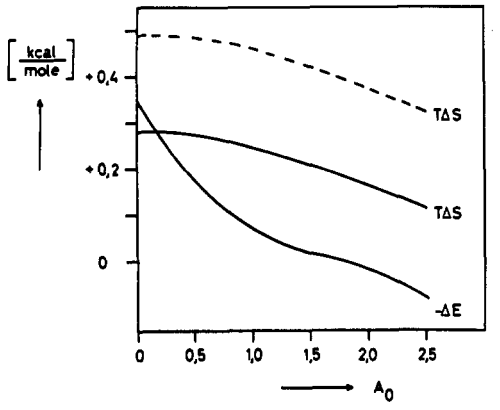

Figure 9. Entropy and energy differences for the potential functions of Figure 10, $t = 130°$ (values for $E_2(\varphi)$, with $E_0 = 4$ kcal, relative to the values for $E_1(\varphi)$, (——) with $E_0 = 4$ kcal, (- - - - -) with $E_0 = 6$ kcal).

mental data for syndiotactic configurations and lower for isotactic configurations. $\Delta\varphi > 5°$ is compatible with experimental results only for chains with high tacticities, if it is assumed that η is clearly lower than unity and that the second-order parameters are lower than those of Figure 6. As stated above, such a combination of parameter values does not agree with the experimental results for atactic configurations.

For two most realistic combinations of parameter values calculations have been carried out for 400 monomer units instead of 100. The characteristic ratios obtained from this are increased a few per cent and agree satisfactorally with the experimental results (see Figure 7). For the same parameter sets, the temperature coefficients of the unperturbed dimensions, d ln $\langle r_0^2\rangle$/dT, have been evaluated. To this purpose the statistical weights have been transformed to their values at 100°. $\langle r_0^2\rangle/nl^2$ has been calculated with the random number sequences generated for 130°.

The temperature coefficient d ln $\langle r_0^2\rangle$/dT is dependent on the energy differences of the rotational isomeric states as well as on the entropy differences, which may be caused by different shapes of the potential walls. In the following the free energy differences ΔF and their entropy contributions are calculated with the approximation of classical statistical mechanics[8] by integrating over a bond rotation angle φ. If the bar-

(8) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Interscience, New York, N. Y., 1963, Chapter 2.

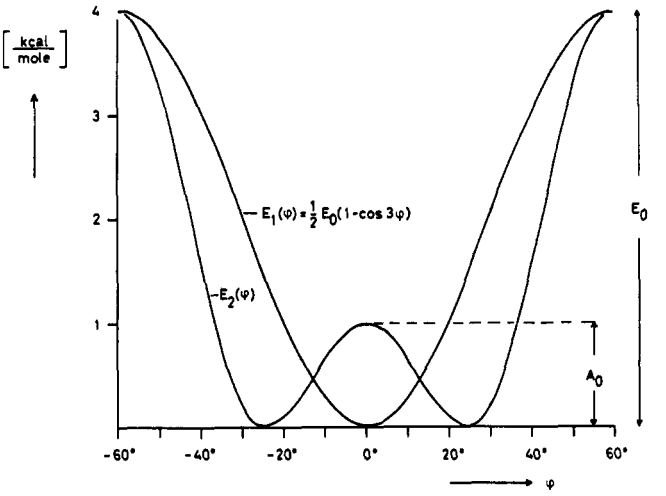

Figure 10. Potential curves for estimating the entropy contributions to the statistical weights (for the analytical expression of the double-minima curve, see J. N. Majerus, *J. Polym. Sci., Part A-1*, **8**, 1737 (1970).)

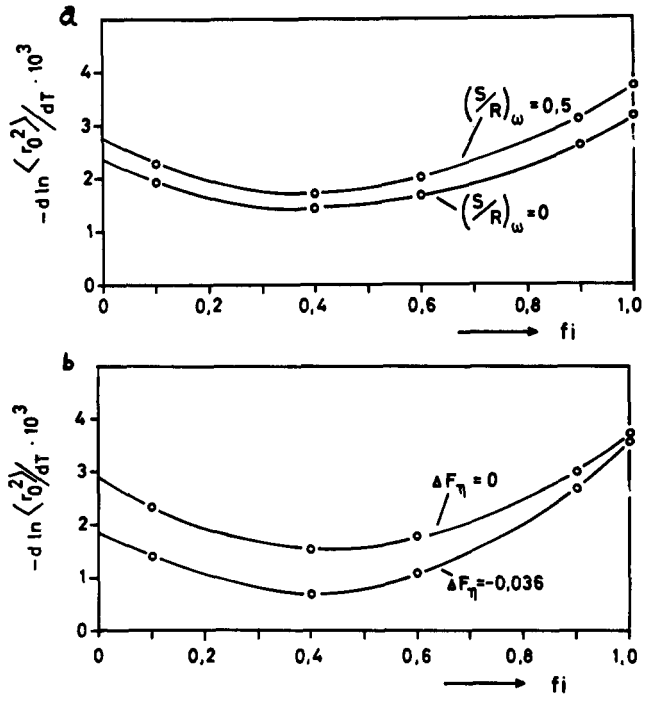

Figure 11. Temperature coefficients of the characteristic ratios; 100 monomer units, $\tau = 0.6$, $\omega' = 0.0565$: (a) $\varphi = 0°$, $\eta = 1$, $\omega = 0.1056$ ($(S/R)_\omega$ characterizes the entropy part of ω and ω'); (b) $\varphi = 5°$, $\eta = 0.9$, $\omega = 0.0932$, $(S/R)_\omega = 0.5$, ($\Delta F_\eta = F_\eta(130°) - F_\eta(100°)$, in kcal).

rier E_0 for the function $E = {}^1/_2E_0(1 - \cos 3\varphi)$ is varied, the differences ΔF are mainly due to the entropy contribution $T\Delta S$ (see Figure 8). Double minima in the angular range of an isomeric state in the Flory model lead to an increase of entropy. This is demonstrated in Figure 9, which presents ΔF and $-\Delta E$ for the two potential curves in Figure 10.

Since by semiempirical energy calculations on *n*-pentane[2,3] double minima have been found for the states with second-order interactions, the free energies F_ω and $F_{\omega'}$ may include a positive entropy contribution. The assumption $(TS)_\omega = (TS)_{\omega'} = 0.4$ kcal leads to a more pronounced temperature dependence of $\langle r_0^2\rangle/nl^2$ (see Figure 11a) and improves the

agreement with the experimental value, -4.09×10^{-3} deg^{-1}, of Nakajima and Saijyo[9] for isotactic configurations. Hamada,[10a] however, has found a considerably lower temperature coefficient, -1.5×10^{-3} deg^{-1} (unpublished results). Therefore, at the moment a final conclusion about the entropy contributions to F_ω and $F_{\omega'}$ cannot be made. For atactic polypropylenes the experimental value[10b] -1.7×10^{-3} deg^{-1} is in good agreement with the lower calculated curve in Figure 11a.

The free energies of the rotational isomeric states are generally dependent on the solvent too.[13] If small changes of one free energy, F_η, for example, have essential influence on the unperturbed dimensions, the temperature coefficients derived from measurements in different θ solvents may vary to a great extent. Such an effect has been simulated in Figure 11b. The free energy F_η for 130° has been assumed to be only 0.036 kcal lower than the corresponding F_η at 100°. The temperature coefficients derived in this way decrease up to the half of their original values.

Conclusion

The unperturbed dimensions of polypropylenes can be described by second-order energies, which are quite the same as the corresponding energy for polymethylene. Then the positions of the bond rotation angles in the three-state model of Flory do not deviate more than a few degrees from planar trans and symetrically staggered gauche. In this way good agreement can be obtained with the experimental data for all tacticities, whereas the parameters of Abe,[11] basing on higher second-order energies than ours, have given much higher values for syndiotactic configurations.

With the comparably low second-order energies, the unperturbed dimensions of "isotactic" polypropylenes are only slightly dependent on the content of syndiotactic dyads. The temperature coefficient is also less sensitive to the fraction of syndiotactic dyads. Consequently, the open question about the exact fraction of syndiotactic dyads in "isotactic" polypropylenes—as derived from nmr[12,14]—is of only minor importance for the comparison of the calculated and measured unperturbed dimensions. This agrees with the conclusion of Boyd and Breitling[15] derived from conformational calculations on polypropylenes.

Acknowledgment. We thank Deutsche Forschungsgemeinschaft for financial support. To Dr. E. Klesper we are greatly indebted for fruitful discussions.

(9) A. Nakajima and A. Saijyo, *J. Polym. Sci., Part A-2*, **6**, 735 (1968).
(10) (a) Hamada, cited by Abe and Flory, see ref 11 and 12; (b) F. Danusso, and G. Morajlio, *Ist. Lombardo, Rend. Sci. A*, **93**, 666 (1959); G. Morajlio and G. Gianotti, *Eur. Polym. J.* **5**, 787 (1969).
(11) A. Abe, *Polym. J.*, **1**, 232 (1970).
(12) P. J. Flory, *Macromolecules*, **3**, 613 (1970).
(13) S. Lifson and I. Oppenheim, *J. Chem. Phys.*, **33**, 109 (1960).
(14) F. Heatly, R. Salovey, and F. A. Bovey, *Macromolecules*, **2**, 619 (1969).
(15) R. H. Boyd and S. Breitling, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **13**, 342 (1972).

Stress-Optical Behavior of Polymethylene and Poly(dimethylsiloxane)

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ABSTRACT: The strain birefringence of polymethylene (PM) and for poly(dimethylsiloxane) (PDMS) networks, unswollen and swollen with diluents, has been investigated over the temperature ranges 115–220° and 15–90°, respectively. Temperature coefficients of the optical-configuration parameter, Δa, have been determined with much improved accuracy by cycling the temperature at fixed length rather than, as heretofore, by determining stress-birefringence isotherms at a series of temperatures. Dilution of PM with decalin reduces $-10^3 \mathrm{d} \ln \Delta a/\mathrm{d}T$ from 3.8 (±0.1) to 1.4 (±0.1) deg^{-1}. The latter value is virtually coincident with calculations from rotational isomeric state theory. From $\Delta a = 4.0 \times 10^{-24}$ cm^3 in decalin at 150° theory yields $\Gamma_{PM} \equiv \Delta\alpha_{CC} - 1.88\Delta\alpha_{CH} = 1.0 \times 10^{-24}$ cm^3 (where $\Delta\alpha$'s are bond optical anisotropies) compared with 0.56×10^{-24} cm^3 from depolarized scattering by *n*-alkanes in CCl_4. Residual intermolecular correlations in the PM–decalin system are suggested as responsible for the discrepancy. Swelling of PM with *n*-$C_{12}H_{26}$ and *n*-$C_{22}H_{46}$ effects smaller reductions in Δa and $-\mathrm{d} \ln \Delta a/\mathrm{d}T$. For PDMS, the value of Δa is markedly reduced by swelling with decalin, with cyclohexane, and especially with CCl_4. In CCl_4, $\Delta a = 0.18 \times 10^{-24}$ cm^3 at 70°, giving $\Gamma_{PDMS} \equiv \Delta\alpha_{SiO} - \Delta\alpha_{SiC} + \Delta\alpha_{CH} = 0.047 \times 10^{-24}$ cm^3. The observed (positive) temperature coefficient considerably exceeds theoretical predictions, and would be at variance with the supposition of order in the amorphous polymer. The vanishingly small optical anisotropy of PDMS casts doubt on the significance of the discrepancy with theory.

This investigation was prompted by evidence indicating the stress-optical behavior of cross-linked networks to be at variance with calculations according to rotational isomeric state schemes successfully used to treat other configuration-dependent properties of polymer chains.[1] In particular, the experimental temperature dependence of the stress-optical coefficients for cross-linked amorphous polymethylene[2,3] (PM) and for poly(dimethylsiloxane)[4,5] (PDMS) have been

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.
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(3) D. W. Saunders, D. R. Lightfoot, and D. A. Parsons, *ibid.*, **6**, 1183 (1968).
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