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Stereochemical Equilibrium and Configurational Statistics in Polystyrene and Its Oligomers

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Abstract: Mixtures of diastereoisomers of 2,4,6-triphenylheptane (TPH) have been epimerized in dimethyl sulfide (DMSO) containing *t*-BuOK. The mole fractions of isotactic, heterotactic, and syndiotactic isomers at equilibrium at 70° are 0.217, 0.499, and 0.284, respectively. These results, in conjunction with the ratio 0.48/0.52 previously reported for the *meso* and racemic 2,4-diphenylpentanes (DPP) at equilibrium at 25°, are interpreted according to the theory of stereochemical equilibrium. Proportions of various conformers in individual DPP and TPH isomers estimated from nmr coupling constants by Bovey and coworkers and by Pivcová and collaborators are interpreted similarly in terms of interactions associated with various conformations. The theory of equilibria between isomers and the associated theory of the conformer populations for each isomer provide a mutually consistent interpretation of the two kinds of results, the same arbitrary parameters (two in number) being used for both. Stereochemical equilibria and conformer populations calculated for polystyrene from the same parameters differ considerably from those for the oligomers. Deuterium exchange with the α -hydrogens in polystyrene has been demonstrated by base catalysis in *d*₆-DMSO.

The conformations accessible to a vinyl polymer chain $H-(CH_2CHR)_x-CH_3$, in which R is a large group such as C_6H_5 , are severely limited by steric interactions. The effects of these nonbonded interactions on the conformations of the chain skeleton depend on the stereochemical configurations of the succession of asymmetric centers CHR. The over-all stereochemical configuration of a vinyl polymer chain is conveniently described by the sequence of *meso* (*m*) and racemic (*r*) dyads $-CHR-CH_2-CHR-$. The chemical bonding in each diastereoisomeric molecule thus defined is identical, apart from the geometrical differences cited. From a thermodynamic point of view, the isomers differ from one another only through differences in the nonbonded interactions associated with the various conformations of each isomer. The state of equilibrium, established in the presence of a suitable catalyst permitting isomerization (epimerization) of the asymmetric centers, must reflect these differences and these differences alone. Thus, the mole fractions of diastereoisomeric species comprising the equilibrium mixture should be determined by the same nonbonded interactions operative in

a given diastereoisomer, and reflected therefore in the incidence of various conformers in each diastereoisomer.²

The conformations generated by rotations about bonds of the chain are conveniently treated in terms of discrete rotational states, generally chosen to coincide with minima in the rotational potential. For C-C bonds, these ordinarily are represented by *trans* and *gauche* states situated at rotations approximated by 0, +120, and -120°, measured from the *trans* conformation. They are designated *t*, *g*⁺, and *g*⁻, respectively. The description of molecular conformations in these or similar terms has widespread precedence, not only for polymeric chains but also for smaller molecules capable of rotational isomerism.

A system of statistical weight factors for various local conformations of vinyl chains has been put forward, and a procedure has been established for combining these factors systematically to generate the statistical weight applicable to any given conformation of a vinyl

(1) From the dissertation submitted by A. D. Williams in fulfillment of the requirements for the Ph.D. degree, Stanford University, 1968.

(2) Study of the equilibria between *cis* and *trans* isomers of substituted cyclic compounds has proved to be an especially effective means for evaluation of conformational interactions; see, for example, E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **88**, 5039 (1966); **90**, 3444 (1968); also, F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, **23**, 3147 (1967).

polymeric chain of any prescribed stereochemical sequence and length x .^{3,4} In particular, the partition sum of the statistical weights for each and every conformation of the given chain may be readily generated by straightforward mathematical methods. Various average properties may be deduced in standard fashion from the partition function, or sum. If stereochemical equilibrium prevails, then it is necessary to extend the sum over all diastereoisomeric species, a task which is easily handled by simple mathematical methods,⁵ the prodigious number of such species when x is large notwithstanding. The set of statistical weight factors required is generally small.

Stereochemical equilibrations of 2,4-dimethylglutaric acid and of 2,4,6-tricarboxyheptane, and of their methyl esters, have been carried out by Clark.⁶ His results on the mole fractions of isomers at equilibrium in these dimeric and trimeric oligomers of poly(methyl acrylate) were interpreted⁵ in terms of the theory cited above. Arbitrary assignment of two statistical weight parameters was required. The proportions of various conformations in the individual species as estimated by Doskočilová, Sýkora, Pivcová, Obereigner, and Lím⁷ from nmr coupling constants were similarly interpreted according to theory, the same two parameters being used. The respective values of these parameters determined from the two independent sets of results, obtained by the experimentally unrelated methods cited, were in good agreement.⁵

The epimerization of 2,4-diphenylpentane (DPP) was reported recently.⁸ Equilibration was achieved in solution in dimethyl sulfoxide (DMSO) containing potassium *t*-butoxide.⁹ The ratio of *meso* to racemic isomers at equilibrium yielded a value for one of the parameters. A second one is required for representation of higher homologs, including polystyrene.

In this paper we report results on the equilibration of 2,4,6-triphenylheptane (TPH), the trimeric oligomer of polystyrene. The results thus obtained permit an evaluation of the second parameter required for interpretation of the entire series of homologs. They are correlated with conformational analyses of *meso* and racemic DPP¹⁰ and of isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) TPH¹¹ carried out on the basis of the nmr spectra of the separated diastereoisomers. Exploratory studies aimed at the stereochemical equilibration of polystyrene also are reported.

Experimental Methods

4,6-Diphenylheptanone-2. An ether solution of 2-phenylpropyl bromide (30 g, 0.15 mole) was saturated with CuI at 0°. ¹² 4-Phenyl-

3-buten-2-one (22 g, 0.15 mole) dissolved in 25 ml of ether was added dropwise with vigorous stirring. After standing for 20 min, the solution was poured into 1 l. of saturated ammonium chloride. Solids were removed by filtration, the solution was extracted with ether, and the organic layer was separated and dried over magnesium sulfate. The ether was then removed. Column chromatography was used to separate 3.9 g (0.015 mole) of 4,6-diphenylheptanone-2.

2,4,6-Triphenylheptane. The combined fractions of 4,6-diphenylheptanone-2 were added to an ether solution of phenylmagnesium chloride. The solution was refluxed for 2 hr, then decomposed with dilute sulfuric acid. The organic layer was washed with sodium bicarbonate and dried over magnesium sulfate. After evaporation of the ether, the mixture of 2,4,6-triphenylheptanol-2 and 2,4,6-triphenylheptene-2 was added to a suspension of 0.25 g of palladium-on-carbon catalyst (10% Pd) in 125 ml of ethanol containing 2 ml of concentrated perchloric acid. The mixture was hydrogenated in a Parr bomb for 24 hr at room temperature under a pressure of about 3 atm. The catalyst was removed by filtration and the solution was rinsed twice with water and extracted with ether. Evaporation of the ether layer yielded 1.6 g (0.0053 mole) of 2,4,6-triphenylheptane.

The product was further purified and the three diastereoisomers were partially separated by use of a Varian Aerograph A90-P3 chromatograph. The column, 150 × 0.60 cm packed with 20% by weight SE-30 on Chromosorb W, was operated at 210° with a helium flow rate of 80 ml/min.

Polystyrene. Atactic polystyrene of low molecular weight, *i.e.*, $\bar{M}_n = 2050$, and of narrow distribution was purchased from the Pressure Chemical Co., Pittsburgh, Pa. The ratio of its weight- to number-average molecular weights was reported to be $\bar{M}_w/\bar{M}_n \leq 1.10$.

Equilibration Procedure. Epimerization of TPH was carried out in a DMSO solution containing potassium *t*-butoxide at a concentration of 0.6–1.7 *M*. Mixtures were prepared in a closed system under high vacuum according to procedures developed by Brauman and Nelson.¹³ The DMSO was distilled onto potassium *t*-butoxide. The resulting solution was filtered, then transferred in 2–3-ml portions to ampoules containing approximately 100 mg of the hydrocarbon. The ampoules were chilled with liquid nitrogen and then sealed under vacuum. After warming gradually to room temperature, the ampoules were placed in a constant-temperature bath for specified periods of time. They were opened, the base was destroyed with water, and the hydrocarbon was extracted with *n*-pentane and analyzed.

The insolubility of polystyrene in DMSO necessitated modification of the procedure as follows. A sample of 100 mg of the atactic polystyrene of low molecular weight was first dissolved in 0.5–1.0 ml of benzene. A 2–3-ml portion of the carbanion solution was added, and the ampoule containing the mixture was frozen in liquid nitrogen, evacuated, and sealed. After gradual warming to room temperature, the set of ampoules thus prepared was placed in a thermostat at 70°. The solutions appeared to be homogeneous after several hours. The presence of a faint color, initially pink and turning to violet later, indicated the presence of the benzyl anion. After several weeks at 70°, the ampoules were opened, the base was destroyed with water, and the polymer was extracted with benzene. Nmr spectra of the recovered polymer revealed the presence of a trace impurity, believed to be a product formed from the butoxide. Purification of the polymer by column chromatography¹⁴ eliminated the impurity.

Isotactic polystyrene¹⁵ having a molecular weight (\bar{M}_n) of about 30,000 proved insoluble in DMSO–benzene mixtures even at a volume ratio of 1:1. A higher proportion of benzene rendered the base insoluble and hence could not be used. Experiments with the isotactic polymer therefore were abandoned.

Gas Chromatographic Analysis. Quantitative determinations of the isomers of TPH were carried out using a Varian Aerograph A90-P3 chromatograph equipped with a column, 100 × 0.30 cm, packed with 10% Apiezon L on Chromosorb W. The best separation was achieved at 220° with a helium flow rate of 80 ml/min. The syndiotactic isomer (*rr*) appeared as the first fraction, the heterotactic (*mr*) as the second, and the isotactic (*mm*) as the third. Identities of the isomers were confirmed by their nmr spectra as previously reported by Lím and coworkers.¹⁶ The same order of ap-

(3) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, Inc., New York, N. Y., 1969.

(4) P. J. Flory, J. E. Mark, and A. Abe, *J. Amer. Chem. Soc.*, **88**, 639 (1966).

(5) P. J. Flory, *ibid.*, **89**, 1798 (1967).

(6) H. G. Clark, *J. Polym. Sci., Part C*, 3455 (1968).

(7) D. Doskočilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lím, *ibid.*, 365 (1968).

(8) A. D. Williams, J. I. Brauman, N. J. Nelson, and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 4807 (1967).

(9) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(10) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

(11) H. Pivcová, M. Kolínský, D. Lím, and B. Schneider, submitted for publication. We are indebted to these authors for providing us with a copy of their manuscript in advance of publication.

(12) H. O. House, W. L. Respass, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(13) N. J. Nelson, Ph.D. Thesis, Stanford University, 1967.

(14) T. Altares, Jr., D. P. Wyman, and V. R. Allen, *J. Polym. Sci., Part A*, **2**, 4533 (1964).

(15) Obtained through the courtesy of Dr. D. B. Miller of the Stanford Research Institute, Menlo Park, Calif.

pearance occurred on the column used (see above) for achieving a partial separation of the original synthetic TPH.¹⁷

Experimental Results

Establishment of equilibrium between the *meso* and racemic isomers of 2,4-diphenylpentane (DPP) was achieved, as reported in a previous publication,⁸ after 14 days at room temperature in the presence of *t*-BuOK at concentrations of 0.5–1.0 *M* in DMSO. Preparation of DPP solutions *in vacuo*, following the procedure adopted here for TPH solutions in order to suppress contamination by oxygen and moisture, was not required. In the present investigation, on the other hand, the isomer ratio for a solution of TPH in DMSO with 1.7 *M t*-BuOK prepared under atmospheric conditions was found to have undergone only a small change after 84 days at room temperature. A solution prepared *in vacuo* by the procedure set forth above and kept at room temperature for 28 days likewise exhibited only a small alteration in isomer composition. At a temperature of 70°, however, solutions prepared *in vacuo* approached equilibrium within about 28 days, according to the results given in Table I.

Table I. Epimerization of 2,4,6-Triphenylheptane

Anion concn, <i>M</i>	Time in days (70°)	F_I	F_H	F_S
Sample 1				
0	0	0.312	0.505	0.183
0.6	21	0.218	0.498	0.284
0.8	35	0.215	0.498	0.287
Sample 2				
0	0	0.088	0.506	0.406
0.6	35	0.217	0.499	0.284
0.8	70	0.218	0.499	0.283

The two samples for which data are presented in Table I were partially fractionated by gas chromatography (see above). The initial ratio F_S/F_I of syndiotactic (*rr*, or *dld*) to isotactic (*mm*, or *ddd*) isomers is less than the equilibrium value for sample 1, and greater than the equilibrium value for sample 2. The initial fraction F_H of heterotactic isomer (*mr*, or *ddl* and *lld*) is near the equilibrium mole fraction in both samples. Each result given in Table I is the mean of gas chromatographic analyses carried out in triplicate, the individual analyses agreeing within $\pm 0.5\%$. Final compositions for the two samples after 21–70 days at 70° are in excellent agreement, thus demonstrating the establishment of stereochemical equilibrium. Mean values are $F_I = 0.217$, $F_H = 0.499$, and $F_S = 0.284$, with deviations of less than ± 0.003 .

The diphenylpentane was found⁸ to contain 48.4% of the *meso* isomer at equilibrium at 25°, according to gas chromatographic analysis. Integrated intensities in the nmr spectrum (100 Mc) gave $47 \pm 1\%$ *meso*. From these results we take the fraction f_m of *meso* isomer to be

(16) D. Lím, M. Kolínský, J. Petránek, D. Doskočilová, and B. Schneider, *J. Polym. Sci., Part B*, **4**, 645 (1966).

(17) Retention times of the different isomers on these columns correspond to those found for a known sample of TPH kindly made available to us by Dr. D. Lím of the Institute of Macromolecular Chemistry, Prague. The nmr spectra of the three separate diastereoisomers obtained by us agree with those published by Lím and co-workers.^{11, 16}

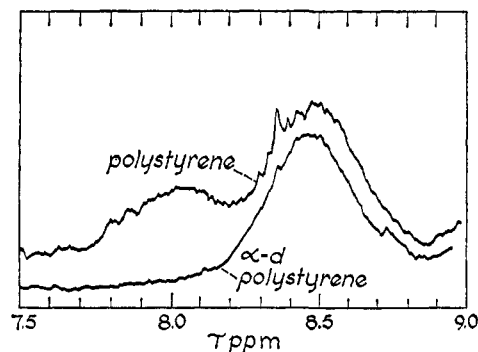


Figure 1. Comparison of 100-Mc nmr spectra of polystyrene before and after deuteration at the α carbons.

0.480 ± 0.005 at 25°. The epimerization of TPH appears to be much slower than of DPP, according to the evidence cited.

Samples of low molecular weight atactic polystyrene ($\bar{M}_n = 2050$) were treated using d_6 -DMSO following the procedure described in the Experimental Section. The nmr spectrum of the polymer recovered after 56 days at 70° and purified by column chromatography (see above) is compared in Figure 1 with the spectrum of the original polymer. The α -proton resonances in the vicinity of τ 8 are reduced by deuteration below the limits of detection in the undeuterated polymer. Samples treated similarly at 25° showed little change over the same period of time. Studies of analogous low molecular compounds subjected to similar conditions indicate racemization to proceed simultaneously with deuterium exchange.⁹ Hence, the stereochemical configuration of the polystyrene may be presumed to have been equilibrated simultaneously with deuteration.

The 220-Mc nmr spectrum of the α -deuterated, and presumably equilibrated, polystyrene is shown in Figure 2 in the region of the methylene (CH_2) resonances.¹⁸ The spectrum was taken on a 5% solution of the polymer in dichlorobenzene at 150°. The spectrum gives evidence of structure, but the poorly resolved peaks do not meet the requirements for quantitative characterization of the stereochemical structure of the equilibrated polymer. The inadequacy of the nmr spectrum of poly- β,β -deuteriostyrene for this purpose has been noted by Brownstein, Bywater, and Worsfold.¹⁹

Theory

The stereochemical configuration of the chain as a whole is adequately defined for our purposes by specification by the *meso* (*m*) or racemic (*r*) character of each dyad $-\text{CHR}-\text{CH}_2-\text{CHR}-$; explicit differentiation of the two racemic forms, *dl* and *ld*, is not required. Statistical weight matrices $U_m^{(2)}$ and $U_r^{(2)}$ may be defined for the respective kinds of dyads.^{3, 5, 20} The partition function for the chain of specific stereochemical sequence is given by

$$Z = \mathbf{J}^* \left(\prod_{k=1}^{x-1} \mathbf{U}_k^{(2)} \right) \mathbf{J} \quad (1)$$

(18) We are indebted to Varian Associates, Palo Alto, Calif., for taking this spectrum on their 220-Mc instrument of advanced design.

(19) S. Brownstein, S. Bywater, and D. J. Worsfold, *J. Phys. Chem.*, **66**, 2067 (1962).

(20) P. J. Flory and Y. Fujiwara, *Macromolecules*, in press.

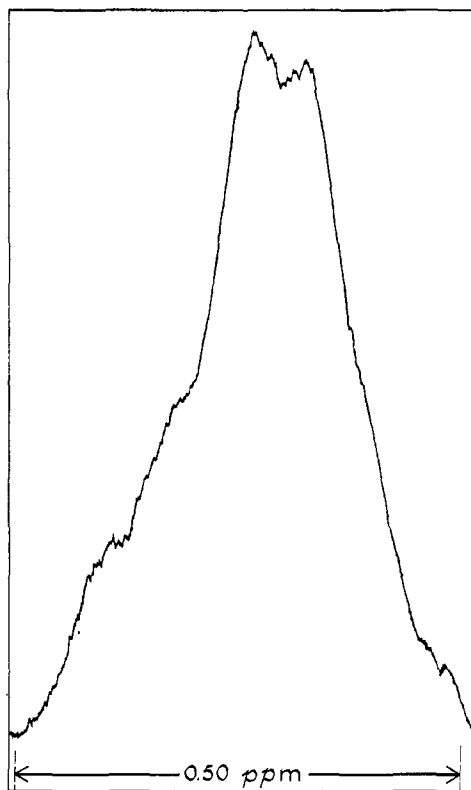


Figure 2. Nmr spectrum, 220 Mc, in the region of the methylenic proton resonances in α -deuterated polystyrene of low molecular weight in σ -dichlorobenzene at 150° (courtesy of Varian Associates, Palo Alto, Calif.).

where the matrix $U_k^{(2)}$ for the k th dyad is either $U_m^{(2)}$ or $U_r^{(2)}$ according to the character of this dyad, J^* and J are the row and column (eq 2) of orders corresponding

$$\left. \begin{aligned} J^* &= [1 \ 0 \ \dots \ 0] \\ J &= \begin{bmatrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{bmatrix} \end{aligned} \right\} \quad (2)$$

to the number of rotational states chosen to describe the conformations accessible to individual bonds. The dyad matrices may be defined in terms of statistical weight matrices U' and U'' for the respective bonds $CHR-CH_2$ and CH_2-CHR of the dyad pair. Thus^{3,5}

$$U_m^{(2)} = U' U_m'' \quad (3)$$

$$U_r^{(2)} = U' U_r'' \quad (4)$$

With the usual assignment of three rotational states, one *trans* (t) and two *gauche* (g and \bar{g}), to each bond, the bond statistical weight matrices take the forms²⁰ shown in eq 5-7.²¹ In each of these matrices, rotational

$$U' = \begin{bmatrix} \eta\tau^* & 1 & \tau \\ \eta & \omega & \tau \\ \eta & 1 & \tau\omega \end{bmatrix} \quad (5)$$

$$U_m'' = \begin{bmatrix} \eta\omega'' & 1 & \tau\omega' \\ \eta & \omega & \tau\omega' \\ \eta\omega' & \omega' & \tau\omega\omega'' \end{bmatrix} \quad (6)$$

(21) The matrices U' , U_m'' , and U_r'' as here defined correspond to those of the same designations in ref 3, but differ from them in the ordering of rows and columns. Either set meets the requirements of eq 1.

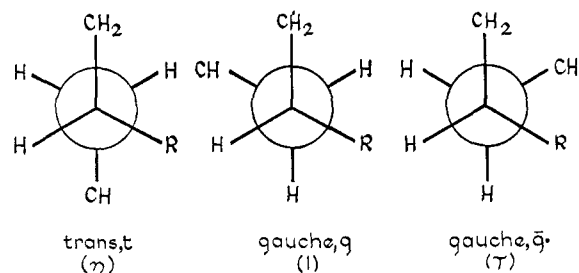


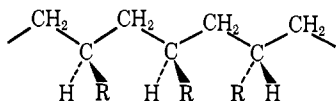
Figure 3.

states t , g , and \bar{g} for the preceding bond are indexed on rows; corresponding states for the bond in question are indexed in the same order on the columns. The significations of these designations are defined by the Newman projections in Figure 3. For asymmetric

$$U_r'' = \begin{bmatrix} \eta & \omega' & \tau\omega'' \\ \eta\omega' & 1 & \tau\omega \\ \eta\omega'' & \omega & \tau\omega'^2 \end{bmatrix} \quad (7)$$

centers having the configurations of those shown, g and \bar{g} denote right- and left-handed rotations, respectively. The mirror image of each diagram is to be included, however, under the same designation. Mirror reflection inverts the asymmetric center and reverses the sign of rotation as well. Hence, neither g nor \bar{g} can be identified with rotations of a given sign; such a stipulation can be made only if the symmetry of the asymmetric center is specified. Rather, the states designated t , g , and \bar{g} are distinguished by the interactions that obtain in each. The interactions of course are unaltered by mirror reflection. The same statistical weight factor is therefore applicable to both members of a mirror-image pair. The statistical weight factors that take account of interactions of "first order," *i.e.*, interactions that depend on only one skeletal bond rotation, are given in parentheses in Figure 3 for each conformation. These interactions involve pairs of groups (CH_2 , CH , or R) separated by three bonds. The factor η is introduced for each conformation in which the substituent R is *gauche* with respect to a CH group separated from it by three skeletal bonds. This statistical weight is assigned relative to a value of unity for a CH_2 group similarly situated with respect to CH . A factor τ (usually <1) is introduced for the conformation in which both CH_2 and R are *gauche* with respect to CH . The factor τ^* takes account⁴ of constraints imposed on rotations about the $CH-R$ bond if R is an articulated substituent such as $-CH_2CH_3$ or $-O-CH_3$, etc. These constraints, involving interactions with neighboring CH groups of the chain skeleton, are operative when both skeletal bonds adjoining the central CHR group are *trans*.^{3,4} For a symmetric group such as CH_3 , τ^* may be set equal to unity. A value less than unity should be required for an articulated substituent. Inasmuch as the first dyad of the chain is not subject to the constraint considered, we may take $\tau^* = 1$ for the first unit in any case.

The factors ω , ω' , and ω'' pertain to interactions of "second order," which depend on rotations about two consecutive skeletal bonds and involve groups separated by four bonds. The several kinds of interactions in this category can be envisaged by considering the vinyl chain in its planar conformation shown below



and the various conformations generated from this one through rotations about consecutive pairs of skeletal bonds. The factor ω refers to four-bond interactions involving a pair of CH_2 or CH groups, ω' characterizes the interactions between CH_2 and R , and ω'' refers to R interacting with R . These interactions are generally large and conformations subject to them are strongly disfavored. In previous treatments^{3-5, 20} a single parameter ω was used to represent all of them. Separate designation of the three ω 's will be required in the paper which follows, and will find incidental application herein as well.

If stereochemical equilibrium prevails, all combinations of *meso* and racemic dyads are admissible and the relevant partition function Z comprises the sum of the Z 's for each such combination of stereochemical configurations of the chain as a whole. This sum is generated identically by replacement of $U_k^{(2)}$ in eq 1 by the sum of $U_m^{(2)}$ and $U_r^{(2)}$. Thus⁵

$$Z = \mathbf{J}^* \mathfrak{u}_1 \mathfrak{u}^{z-2} \mathbf{J} \quad (8)$$

where

$$\mathfrak{u} = U_m^{(2)} + U_r^{(2)} \quad (9)$$

The first factor, namely \mathfrak{u}_1 , is written separately in eq 8 since $\tau^* = 1$ therein.

The fraction of dyads which are *meso* at equilibrium is given by

$$f_m = 1 - f_r = (x - 1)^{-1} Z^{-1} [\mathbf{J}^* \mathbf{0}] \hat{\mathfrak{u}}_1 \hat{\mathfrak{u}}^{z-2} \begin{bmatrix} \mathbf{0} \\ \mathbf{J} \end{bmatrix} \quad (10)$$

where

$$\hat{\mathfrak{u}} = \begin{bmatrix} \mathfrak{u} & U_m^{(2)} \\ \mathbf{0} & \mathfrak{u} \end{bmatrix} \quad (11)$$

The fractions F_I , F_H , and F_S of isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triads have been obtained through elaboration of this method.⁵ Thus, the fraction of triads which are isotactic at stereochemical equilibrium is given by

$$F_I = Z^{-1} (x - 2)^{-1} \mathbf{J}^* \times [U_m; i_1^{(2)} \quad U_r; i_1^{(2)} \quad \mathbf{0} \quad \mathbf{0}] \hat{\mathfrak{W}}_I^{(z-2)} \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{J} \\ \mathbf{J} \end{bmatrix} \quad (12)$$

where

$$\hat{\mathfrak{W}}_I = \begin{bmatrix} \tau^{\mathfrak{W}} & \tau^{\mathfrak{W}'_I} \\ \mathbf{0} & \tau^{\mathfrak{W}} \end{bmatrix} \quad (13)$$

with

$$\tau^{\mathfrak{W}} = \begin{bmatrix} U_m^{(2)} & U_r^{(2)} \\ U_m^{(2)} & U_r^{(2)} \end{bmatrix} \quad (14)$$

and

$$\tau^{\mathfrak{W}'_I} = \begin{bmatrix} U_m^{(2)} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \quad (15)$$

The *a priori* probabilities F_H and F_S for heterotactic and syndiotactic triads are given by equations identical with eq 12 except for replacement of $\hat{\mathfrak{W}}_I$ by $\hat{\mathfrak{W}}_H$ and $\hat{\mathfrak{W}}_S$, respectively, where

$$\hat{\mathfrak{W}}_H = \begin{bmatrix} \tau^{\mathfrak{W}} & \tau^{\mathfrak{W}'_H} \\ \mathbf{0} & \tau^{\mathfrak{W}} \end{bmatrix} \quad (16)$$

with

$$\tau^{\mathfrak{W}'_H} = \begin{bmatrix} \mathbf{0} & U_r^{(2)} \\ U_m^{(2)} & \mathbf{0} \end{bmatrix} \quad (17)$$

and

$$\hat{\mathfrak{W}}_S = \begin{bmatrix} \tau^{\mathfrak{W}} & \tau^{\mathfrak{W}'_S} \\ \mathbf{0} & \tau^{\mathfrak{W}} \end{bmatrix} \quad (18)$$

with

$$\tau^{\mathfrak{W}'_S} = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & U_r^{(2)} \end{bmatrix} \quad (19)$$

The phenyl substituent that characterizes polystyrene is a comparatively bulky group. Second-order interactions involving a pair of phenyl groups produce severe overlaps, and the virtual suppression of conformations producing such interactions is assured. Hence, we may take $\omega'' = 0$. The second-order interaction (ω') involving C_6H_5 with CH_2 places an aromatic carbon within 1.8 Å of the nearest methylenic hydrogen. This distance, which is about 1.2 Å less than the sum of the van der Waals radii²² of the interacting carbon (1.8 Å) and hydrogen (1.2 Å) atoms, is indicative of a large steric overlap commensurate with that found in the analogous polymethylene interactions.²³ The second-order interaction $\text{CH}_2 \cdots \text{CH}_2$, which has been assigned a weight $\omega = 0.034$ in polymethylene at 25°,²³ places the nearest hydrogens at a distance of 0.9 Å apart. This distance is 1.5 Å less than the sum of the van der Waals radii. The second-order interaction $\text{CH} \cdots \text{CH}$ engenders a corresponding steric conflict. These unfavorable overlaps, both being weighted by ω , can be partially alleviated, however, by slight rotation of the interacting groups. Corresponding rotations are less effective in relieving the $\text{C}_6\text{H}_5 \cdots \text{CH}_2$ repulsion. On this basis we conclude that $\omega' < \omega < 0.05$. In light of these predictions, it is appropriate to let $\omega' = \omega = 0$ for the purposes of the interpretation of results to follow.²⁴

According to elementary considerations of symmetry, the rotation of the phenyl group (R) about the C-R bond should be subject to a sixfold potential in absence of peripheral nonbonded interactions. Pairs of rotational states differing by 180° in angle are indistinguishable. Of the three distinguishable conformations at minima in the bond torsional potential, two are subject to severe steric overlaps; only the one in which the plane of the phenyl group coincides with the plane defined by the H-C-R bond pair is acceptable.

(22) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(23) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).

(24) The replacement of ω and ω' by zero gains support from the indications of semiempirical calculations that τ is in the range $0.1 \leq \tau \leq 0.5$. As more detailed examination of the matrices \mathbf{U}' and \mathbf{U}'' and their performance in the generation of Z will show,³⁻⁵ the factor τ usually occurs in conjunction with the various factors ω in the product expressing the statistical weight for a conformation. Hence, a small value of τ strengthens the justification for replacing the ω 's by zeros.

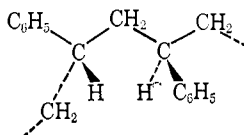
Critical examination of interatomic distances in various allowed conformations of the polystyrene chain skeleton leads one to conclude that it should be virtually free of the interactions peculiar to articulated substituents when *both* of the skeletal bonds adjoining CHR are *trans*. On these grounds, therefore, τ^* could be replaced by unity, and thus eliminated from the scheme of statistical weights. We shall retain τ^* in the equations to follow, however, in order to examine the effects of small departures of it from unity.

The condition $\omega = \omega' = \omega'' = 0$ eliminates all \bar{g} states, and the statistical weight matrices may then be reduced to 2×2 order as follows³⁻⁵

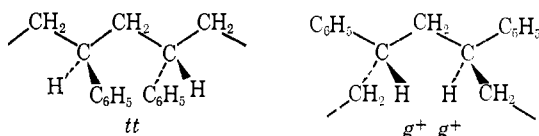
$$U_m^{(2)} = \begin{bmatrix} \eta & \eta\tau^* \\ 0 & \eta \end{bmatrix} \quad (20)$$

$$U_r^{(2)} = \begin{bmatrix} \eta^2\tau^* & 1 \\ \eta^2 & 0 \end{bmatrix} \quad (21)$$

The parameter τ vanishes from the equations when the foregoing conditions are met. The *meso* dyad is restricted to the two *gauche-trans* conformations, *i.e.*, to the g^+t rotational isomer



and its mirror image tg^- . A racemic dyad, under the conditions stated, may assume either of two quite different conformations. These are the *tt* and the *gg* conformations



For the racemic dyad that is shown above, the latter conformer is g^+g^+ ; for its enantiomorph the corresponding form is g^-g^- . The ratio of occurrence of the *tt* and *gg* forms depends on the values of η and τ^* .

In the case of the dimer ($x = 2$), DPP, each *meso* conformer receives a statistical weight η , since one of the phenyl groups is *gauche* with respect to a CH group. On the same basis, the statistical weights for the respective racemic conformers are η^2 and 1, again with $\omega = \omega' = \omega'' = 0$. Hence, the mole fraction of *meso* isomer at equilibrium can be formulated directly with the following result.^{5,8}

$$f_m = 2\eta/(1 + \eta)^2 \quad (22)$$

The mole fractions of the three diastereoisomers of TPH at equilibrium are given by⁵

$$F_I = \eta(2 + \tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (23)$$

$$F_H = 2(1 + \eta^2 + \eta^2\tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (24)$$

$$F_S = \eta(2 + \eta^2\tau^*)/(1 + \eta)^2(2 + \eta\tau^*) \quad (25)$$

when $\omega = \omega' = \omega'' = 0$ is a legitimate approximation. These expressions may be derived from eq 12 to 21, or they may be obtained by enumerating the statistical weight of each conformation of each species through use of the factors defined above.

Discussion

The mole fraction f_m of the *meso* isomer of DPP at equilibrium was found previously³ to be 0.480 ± 0.005 at 25° . It follows from eq 22 that $\eta = 1.5 \pm 0.1$ at 25° .

Compositions of equilibrium mixtures of TPH calculated according to eq 23-25 for several values of η and τ^* are given in Table II. Mole fractions were also

Table II. Ratios of the Three Isomers of 2,4,6-Triphenylheptane at Stereochemical Equilibrium, Calculated According to Eq 23-25

η	τ^*	F_I	F_H	F_S
1.5	1.0	0.206	0.503	0.291
1.5	0.7	0.213	0.506	0.281
1.4	1.0	0.215	0.502	0.283
1.4	0.7	0.220	0.505	0.275
1.2	1.0	0.232	0.501	0.267
Experimental, at 70°		0.217	0.499	0.284

calculated with $\omega = 0.1$ or with $\omega' = 0.1$, using in this case the 3×3 statistical weight matrices of eq 5-7 in conjunction with eq 12-19. Results thus obtained differ by less than 1% from those given in Table II. The simplification resulting from letting $\omega = \omega' = \omega'' = 0$ does not therefore affect the treatment of the results significantly. Mean values of the observed mole fractions, taken from Table I, are quoted in the last row of Table II. Comparison of the calculated mole fractions with those observed at 70° suggests $\eta = 1.4 \pm 0.1$ and $\tau^* = 0.80-1.00$. Improvement in the agreement with experiment gained by a choice of τ^* other than unity is meager at best. A lower value of η compared with that for DPP at 25° is to be expected from evidence presented below on the dependence of η on temperature.

The proportions of various conformers in *meso* and racemic DPP have been estimated by Bovey, Hood, Anderson, and Snyder¹⁰ from nmr coupling constants determined in several solvents (CCl_4 , CS_2 , and $\sigma-C_6H_4Cl_2$) at temperatures from -50 to 200° . Solvent effects could not be detected with certainty; at most, they are very small. Pivcová, Kolínský, Lím, and Schneider¹¹ have determined the nmr spectra of the diastereoisomers of TPH at $20-140^\circ$, and they likewise have estimated the incidences of various conformers from the coupling constants.⁷ The results of these investigations are summarized in the fourth and fifth columns of Table III.

Bovey, *et al.*,¹⁰ found the *meso* isomer to consist exclusively of the *gt* and *tg* (right- and left-handed) conformers, within limits of reliability of the nmr method, throughout the wide temperature range investigated by them. For the racemic diastereoisomers they concluded that the *tt* and *gg* conformers are the principal ones and that all others may be ignored. They found the ratio of *tt* to *gg* conformers to be described by an enthalpy difference $\Delta H = -1.66 \pm 0.2$ kcal mole⁻¹ and by an entropy difference $\Delta S = -3.2 \pm 0.5$ cal mole⁻¹ deg⁻¹. Thus, according to their analysis of nmr coupling constants for racemic DPP

$$p_{tt}/p_{gg} = 0.20 \exp(835/T) \quad (26)$$

where T is the temperature in $^\circ K$. Entries for racemic DPP in the fifth column of Table III have been cal-

Table III. Conformer Ratios in Oligomers of Polystyrene

Oligomer	Conformers	Statistical weights	Temp, °C	Conformer ratios		
				Obsd	Calcd ^c $\tau^* = 1.00$	Calcd ^c $\tau^* = 0.80$
DPP(<i>meso</i>)	<i>tg + gt</i>		35–200	1.00	1.00	
DPP(<i>rac</i>)	<i>tt/gg</i>	$\eta^2/1$	35	0.75/0.25 ^a	0.71/0.29	
			200	0.54/0.46 ^a	0.52/0.48	
TPH(I)	<i>(gtgt + tgtg)/gttg</i>	$2/\tau^*$	70	0.78/0.22 ^b	0.67/0.33	0.71/0.29
			140	0.73/0.27 ^b	0.67/0.33	0.71/0.29
TPH(H)	<i>tggt/gttt/gtgg</i>	$\eta^2/\eta^2\tau^*/1$	20	0.44/0.41/0.15 ^b	0.42/0.42/0.16	0.46/0.37/0.17
			140	0.41/0.34/0.25 ^b	0.37/0.37/0.26	0.39/0.32/0.29
TPH(S)	<i>tttt/(ttgg + ggtt)</i>	$\eta^2\tau^*/2$	20	0.52/0.48 ^b	0.58/0.42	0.52/0.48
			140	0.38/0.62 ^b	0.41/0.59	0.35/0.65

^a From Bovey, Hood, Anderson, and Snyder.¹⁰ Data for DPP(*rac*) have been calculated from the relationship of the ratio to temperature given by these authors. See eq 26. ^b From Pivcová, Kolínský, Lím, and Schneider.¹¹ ^c All calculated ratios have been obtained by use of eq 28 for η .

culated from this relationship, which summarizes the results of Bovey and coworkers.¹⁰ According to our treatment of chain conformations, this ratio may be identified with η^2 , from which it would follow that

$$\eta = 0.45 \exp(417/T) \quad (27)$$

Pivcová and coworkers¹¹ found slightly smaller values for the difference in enthalpy between the *tt* and *gg* forms for a racemic dyad in either the syndiotactic (S) isomer of TPH or in the heterotactic (H) isomer. Mean values of $\Delta H = -1.4 \pm 0.2$ kcal mole⁻¹ and $\Delta S = 2.8 \pm 0.5$ cal mole⁻¹ deg⁻¹ are indicated by the experimental results quoted in Table III for both DPP and TPH. On this basis we take

$$\eta = 0.50 \exp(350/T) \quad (28)$$

Data in the last two columns of Table III have been calculated from values of η given by this equation; calculations for TPH were carried out with $\tau^* = 1.00$ and 0.80 in the respective final columns as indicated. Ratios calculated with $\tau^* = 0.80$ show somewhat better agreement with observed values than those calculated with $\tau = 1.00$, but the marginal improvement is of questionable significance. The agreement in either case probably is within the limits of error of the method of determination, including the approximations involved in the interpretation of nmr coupling constants.

A value of η exceeding unity denotes interactions favoring the *trans* rotational state, in which C₆H₅, rather than CH₂, is *syn* (i.e., *gauche*) with respect to CH. In these terms, eq 28 implies that this conformation is favored by an energy difference $\Delta H_\eta = -700$ cal mole⁻¹, and opposed by an entropy difference $\Delta S_\eta = -1.4$ cal mole⁻¹ deg⁻¹. The higher dispersion interactions of the phenyl group compared to methylene may explain the sign of ΔH . The entropy difference confirms inferences drawn from inspection of models showing rotations of the phenyl group about the C–C₆H₅ bond to be subject to greater constraints when one of the adjoining skeletal bonds is *trans* than when it is *gauche*. In the latter conformation, the phenyl group is exposed to a greater degree and hence impeded to a lesser extent by intramolecular constraints. Similar explanations were put forth by Bovey and coworkers¹⁰ with reference to their conformational analysis of DPP.

According to eq 28, which underlies the calculations of conformation ratios, $\eta = 1.62$ at 25° and 1.39 at 70°, these being the respective temperatures of the

equilibration experiments on DPP and TPH. The former value is somewhat greater than that (1.5) deduced from the *meso*/racemic ratio for equilibrated DPP, but the difference probably is not beyond the limits of experimental error. The value of η at 70° is in good accord with deductions from the similar experiments on TPH carried out at this temperature.

Both stereochemical equilibria and conformation ratios for individual diastereoisomeric species are thus successfully interpreted in terms of a unified theory of intramolecular interactions, a single set of parameters being applied to both sets of experimental results. This constitutes the main achievement of the present investigation. The consistency between calculations and experiment offers strong evidence in support of the rotational isomeric state model for the representation of the conformations of these oligomers of vinyl chains.

The similar equilibration of polystyrene appears feasible in light of the experiments reported above on deuteration of polystyrene at α positions. Unfortunately, suitable analytical methods for determining the dyad (and/or triad) composition are unavailable, and comparison of theory with experiment is not therefore immediately in prospect. The implications, with respect to polystyrene, of results for the dimeric and trimeric oligomers are nevertheless of interest. According to the theory outlined above, the fraction of *meso* dyads in the limit $x \rightarrow \infty$ is given by⁵

$$f_m = 2(1 + \eta\tau^*)/(2 + \eta\tau^*)^2 \quad (29)$$

subject to the condition $\omega = \omega' = \omega'' = 0$. In the same circumstances the equilibrium fractions of various triads are⁵

$$F_I = (3\eta\tau^* + 2)/(\eta\tau^* + 2)^3 \quad (30)$$

$$F_H = [(2\eta\tau^*)^2 + 6\eta\tau^* + 4]/(\eta\tau^* + 2)^3 \quad (31)$$

and of course

$$F_S = 1 - F_I - F_H \quad (32)$$

Illustrative calculations of these quantities for polystyrene at stereochemical equilibrium are presented in Table IV for two temperatures, 20 and 140°. The essential parameter η has been taken from eq 28, and $\tau^* = 1.00$ throughout. Included in the last column for comparison are mole fractions for TPH equilibrated at 140°, calculated according to eq 23–25; the

Table IV. Calculated Dyad and Triad Composition at Stereochemical Equilibrium^a

	Polystyrene 20°	Polystyrene 140°	TPH 140°
f_m	0.398	0.432	0.486
F_I	0.143	0.173	0.235
F_H	0.510	0.518	0.501
F_S	0.347	0.309	0.264

^a All calculations with $\tau^* = 1.00$ and η given by eq 28.

fraction of *meso* dyads in TPH is given by $F_I + 1/2F_H$, i.e., by⁵

$$(f_m)_s = (1 + \eta + \eta\tau^*) / (1 + \eta)(2 + \eta\tau^*) \quad (33)$$

The occurrence of racemic dyads in excess over *meso* dyads is a direct consequence of $\eta > 1$. It is to be noted, however, that the equilibrium composition of the polystyrene chain differs markedly from that of TPH (or of DPP as well). Neighbor influences obviously are responsible for the differences. The fallacy of direct identification of the polymer composition at equilibrium with that of its oligomeric analog will be apparent from the illustrative calculations in Table IV.

In an all-syndiotactic chain of great length ($x \rightarrow \infty$) and subject to the condition $\omega = \omega' = \omega'' = 0$, the proportion of dyads that occur in the *tt* conformation is given by²⁰

$$p_{tt}'' = 1 - 2/[4 + (\eta\tau^*)^2 + \eta\tau^*\sqrt{4 + (\eta\tau^*)^2}] \quad (34)$$

This result may be obtained by application of familiar eigenvalue methods to the matrix $U^{(2)}$ given by eq 21. With η given by eq 28 and $\tau^* = 1.00$, we find according to eq 34 that $p_{tt}'' = 0.818$ at 20° and 0.752 at 140°. In assessing this indicated preference for the *trans* conformation, one should observe that eq 34 yields $p_{tt}'' = 1/2$ in the limit $\eta = 0$, as follows from the rule that neighboring dyads cannot both be *gg* when the ω 's are zero. A strong preference for the *tt* form is nevertheless indicated. This follows directly from the fact that η exceeds unity according to eq 28 at temperatures below about 200°.

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Stereochemical Equilibrium and Configurational Statistics in Oligomers of Poly(vinyl chloride)

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Abstract: Stereochemical equilibration of 2,4-dichloro-*n*-pentane (DCP) in DMSO at 70° in the presence of LiCl yields a mixture containing $36.4 \pm 0.3\%$ of the *meso* isomer. The statistical weight parameter (η) evaluated from this result is used for theoretical calculation of the proportions of various conformers in *meso* and racemic DCP, and also in the three diastereoisomers of 2,4,6-trichloro-*n*-heptane (TCH). Calculations for TCH are compared with estimates of Doskočilová and coworkers from nmr coupling constants. It is shown that the less-favored conformations, often ignored, contribute appreciably to the conformer populations of the TCH isomers.

Molecules of the series $H-(CH_2CHCl)_x-CH_3$, comprising poly(vinyl chloride) and its oligomers, are characterized by less severe steric interactions than the homologs of polystyrene² owing to the smaller size of the chlorine substituent compared with phenyl. Conformations in which a chlorine substituent is involved in a steric overlap with another chlorine atom or with a methylene group cannot therefore be so readily subordinated to the category of near-negligibility. A greater number of conformations must be taken into account, with appropriate weights assigned to each, and a larger set of parameters is required to describe ade-

quately those conformations which make appreciable contributions. The task is by no means beyond reach of fulfillment, and definite inferences can be drawn from analysis of the limited experimental evidence available.

Both infrared and nmr spectroscopy³⁻¹⁰ have been

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