Configurational Studies on Poly-α-methylstyrene

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Received December 3, 1976

ABSTRACT: Energy differences between the various conformational states of the meso and racemic dyads of poly-α-methylstyrene were estimated using semiempirical methods. A crude method of including the conformation-dependent solvent interactions was applied in estimating the energies. The tt state of the racemic dyad is about 1000 cal mol^{-1} lower in energy than that of the meso dyad. The gt state of meso and racemic dyads are almost of equal energy to the meso tt state. The characteristic ratios were calculated for isotactic, syndiotactic, and stereoirregular chains. The calculated values show fair agreement with the experimental results. The temperature dependence of the characteristic ratio for atactic PMS was evaluated and it parallels the experimental observations of Noda et al.

The configurational characteristics of disubstituted vinyl chains, in which R and R′ (Figure 1) are greater in size than hydrogen, are generally different from those of monosubstituted vinyl chains.[1]

In a disubstituted vinyl chain, in which R $\neq$ R′ $\neq$ H, none of the conformations of the bonds i, $i+1$ are free of second-order overlap.[3,4] For the dyad shown in Figure 1, in each of the conformations of the bonds i and $i+1$, two such second-order interactions occur between the members of the set $(CH_2)_{i-2}$, R_{i-1}, R'_{i-1} and those of the set $(CH_2)_{i+2}$, R_{i+1}, and R'_{i+1}. Since none of the conformations is preferred solely on the basis of second-order interactions, interdependance of bond conformations extending up to fourth order may have to be considered, and an elaboration of the statistical weight matrices is required. Instead of formulating the statistical weight matrices for the neighboring bonds as in the treatment of monosubstituted chains, matrices embracing neighboring *bond pairs* have to be formulated.[1] Thus, the conformation of a bond such as $i+1$ would depend not only on the conformation of the bond i, but also on that of the bond $i-1$. The procedure for constructing such statistical weight matrices was presented before[1] and an application of the method was demonstrated for polyisobutylene[2] in which R = R′ = CH_3.

Although the treatment of a disubstituted vinyl chain may seem formidable, its complexity depends very much on the nature of R and R′. The calculations on PMMA (R = $COOCH_3$, R′ = CH_3) showed that the planarity of the ester group imposes severe restrictions on the $\bar{g}$ conformations of the skeletal bonds.[5] This severity cannot be relieved by any reasonable adjustments of the rotations around the bonds. As a consequence, the treatment of the PMMA chains required consideration of only the t and g states of the bonds and the higher order interactions can be neglected. The order of the statistical weight matrices is reduced to 2 × 2, and thus the calculations became simpler than even for a monosubstituted chain such as polypropylene.[6]

Such a decisive deletion of the $\bar{g}$ state owing to the planarity of the side group was found to be applicable also to monosubstituted chains such as polystyrene[7] and poly(methyl acrylate).[8]

The poly-α-methylstyrene (PMS) chain contains two different substituents, R = C_6H_5 and R′ = CH_3. The latter may be considered to be approximately cylindrically symmetric and can be taken to be equivalent to a CH_2 group. The side group R is planar and possesses a twofold symmetry about the C^α–C^β axis. The planarity of the phenyl group can be expected to eliminate the $\bar{g}$ states of the skeletal bonds.

The conformational features of PMS chains are presented here, using the empirical methods to estimate the energy differences between the various states. The proximity of the large phenyl groups, in conformations such as tt of the meso dyad, limits access of solvent molecules to the polymer and particularly to the phenyl groups. The interaction between the polymer and the solvent is therefore dependent on the conformation. An approximate method of including this effect, applied previously to polystyrene,[7] was adopted. The estimated energies are used to calculate the characteristic ratio for stereoregular and stereoirregular chains and its dependence on temperature.

Energy Calculations

A segment of an isotactic PMS chain is shown in Figure 2, with all the skeletal bonds in the trans conformation which defines $\phi_i = 0$ (i = 1 to n). We adhere to the notation of Flory et al.[1] in defining the chirality of the bonds and the sense of rotations. Accordingly, the bond i in Figure 2 belongs to the d species and $i+1$ to the l species. A sequence of |dl|dl| bonds generates the isotactic chain. Here the vertical bars denote the location of the C^α atom. Similarly, the succession of |dd|ll|dd|, etc., generates the syndiotactic chain. Viewing always from the C^α atom to the methylene group, positive increment in ϕ for the d bonds is achieved if the rotation is right handed. For the l bonds, the rotations are performed in the left-handed sense.

The bond lengths and bond angles are given in Table I, and these are similar to those used previously.[5,7] Due to the large size of the phenyl and methyl groups, the angle C^α–C–C^α at the methylene group was taken to be 122°, similar to the value used for PMMA. Energy calculations[5] and the crystallographic data[9] support the choice of such a large value for this angle. The phenyl group was positioned such that its plane bisects the angle CH_2–C^α–CH_2, and the bond C^β–$C^{\gamma'}$ is cis to C^α–CH_3. This defines $\chi = 0$ and any rotation of the phenyl group from $\chi = 0$ was neglected as insignificant.[7]

A threefold intrinsic torsional potential, with a barrier of 2.8 kcal mol^{-1}, was used for rotations around each skeletal bond. The nonbonded interactions were estimated using the Lennard-Jones 6–12 potential function. The parameters employed for the function are given in Table II. The van der Waals radius of the aromatic carbon was taken to be 0.1 Å greater than the "thickness" of the phenyl group in crystal structures.[10] The CH_3 and CH_2 groups were treated as spherical domains of equal size.

Because of the bulkiness and the planarity of the phenyl groups, in a conformation such as tt of the meso dyad in which the phenyl groups interact with each other, the accessibility of the solvent molecules to the polymer is denied. The energy of attraction between the phenyl groups in this conformation is large. As the distance between these groups increases due to rotations ϕ_i and ϕ_{i+1}, the interaction between the phenyl groups decreases and it becomes negligible in the tg or gt conformation. However, the phenyl groups are now in a favorable position to interact with the solvent molecules and this compensates for the reduced interaction between the phenyl groups themselves.

It is expected that beyond a certain distance which is large

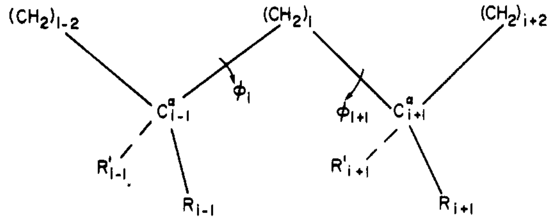

Figure 1. Schematic representation of a vinyl chain.

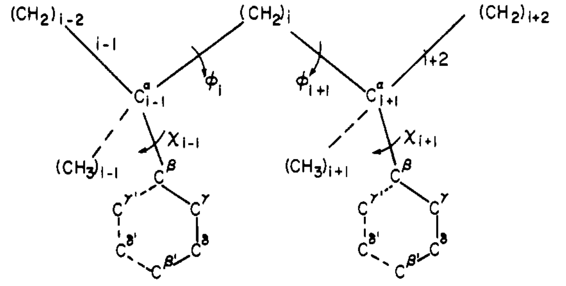

Figure 2. Schematic representation of a segment of isotactic PMS. The rotation angles and the indexing of the bonds are shown.

enough to allow the entry of solvent molecules, the decrease in the interaction between the phenyl groups will be compensated by the interaction of the solvent molecules with the phenyl group. The energy of the system would then level off at this distance. Following Yoon et al.,[7,8] we assume the energy between every pair of atoms, represented by a 6–12 function, to remain constant at the value for $r = \sigma$, for all distances greater than σ. Thus,

$$E_r = E_\sigma \text{ for } r > \sigma \qquad (1)$$

where E is the energy, r is the interatomic distance, and σ is the suitably chosen cut-off distance. The precise value of σ is difficult to determine. Yoon et al.[7,8] examined the effect of various values of σ on the relative energies of the conformations of polystyrene and poly(methylacrylate) chains and concluded that a value of 5 Å is reasonable. The same value is used in the present calculations.[11] It was also found[7,8] that using different values for σ changed the relative energies of the various conformations of the dyads but the location of the minima and the shapes of the energy surfaces surrounding the minima were unaltered.

Results of Energy Calculations

Conformational energies calculated for a meso dyad are given in Figure 3, as a function of the rotation angles ϕ_i and ϕ_{i+1}. Contours are drawn at intervals of 2 kcal mol^{-1} and the energies are expressed relative to the minimum for the tt state. The rotation ϕ_i is measured in the right-handed sense and ϕ_{i+1} in the left-handed sense.

The shape of the contours resembles those presented[5] for PMMA and is perhaps characteristic of a disubstituted vinyl chain. The $\bar{g}$ conformations are of very high energy and no minimum was noted in the neighborhood of the $\bar{g}$ state. This is essentially due to the severe overlap between the planar phenyl group and the groups attached to the adjacent C$^\alpha$ atom. The severity of the interaction remains for any reasonable adjustments of the rotation angle χ. Hence, the $\bar{g}$ state is ruled out from further consideration. This feature was discussed in detail for the cases of PMMA,[5] polystyrene,[7] and poly(methyl acrylate).[8]

Pairs of minima are recorded in the vicinity of permissible staggered conformations: tt, tg, gt, and gg. The displacements of the minima in ϕ_i and ϕ_{i+1}, from perfect staggering, are of opposite sign and are about 20° in magnitude.

Table I
Bond Lengths and Bond Angles Used in This Study

Atoms in bond	Bond length, Å	Atoms in bond	Bond angle, deg
C–C	1.53	CH$_2$–C$^\alpha$–CH$_2$	109.5
C–C^{ar}	1.51	C$^\alpha$–CH$_2$–C$^\alpha$	122
C^{ar}–C^{ar}	1.34	C^{ar}–C^{ar}–C^{ar}	120
C–H	1.10	CH$_2$–C$^\alpha$–C^{ar}	109.5
C$^\alpha$–CH$_3$	1.53	C^{ar}–C^{ar}–H	120

Table II
Parameters Used for Calculating Nonbonded Interaction Energy

Atom or group	Polarizability, α	Effective No. of electrons, N	van der Waals radius, Å
C	0.93	5	1.8
C (aromatic)	1.23	5	1.95
CH$_2$ or CH$_3$	1.77	7	2.0
H	0.42	0.9	1.3

Two symmetrical minima are recorded for the tt state, at (25, −15) and (−15, 25). The energy at the perfectly staggered position, (0, 0), is high. For (ϕ_i, ϕ_{i+1}) = (0°, 0°), the distances $C^\beta{}_{i-1} \cdots C^\alpha{}_{i+1}$, $C^\beta{}_{i-1} \cdots C^{\gamma'}{}_{i+1}$, $C^\beta{}_{i-1} \cdots C^\beta{}_{i+1}$, $C^\gamma{}_{i-1} \cdots C^\gamma{}_{i+1}$, and $C^{\gamma'}{}_{i-1} \cdots C^{\gamma'}{}_{i+1}$ are 3.16, 3.29, 2.87, 2.74, and 3.16 Å, respectively, all of them being less than the sum of the van der Waals radii. For a displacement in ϕ_i and ϕ_{i+1}, e.g., to (25, −15), these distances increase to 3.4, 3.84, 3.15, 3.32, and 3.6 Å, respectively. The distances $C^{\delta'}{}_{i-1} \cdots C^{\delta'}{}_{i+1}$, $C^{\beta'}{}_{i-1} \cdots C^{\beta'}{}_{i+1}$, and $C^\delta{}_{i-1} \cdots C^\delta{}_{i+1}$ which are 3.33, 3.21, and 2.92 Å for (0°, 0°) increase beyond the sum of van der Waals radii for (25, −15). Displacements of the same sign, e.g., (25, 15), decrease the distance between groups and are disfavored. For example, for (ϕ_i, ϕ_{i+1}) = (25, 15), the distance $(CH_3)_{i-1} \cdots (CH_3)_{i+1}$ is 2.5 Å. Shifts of more than 25° in ϕ_i or ϕ_{i+1} are not preferred either. In such a case, the "diagonal interactions" begin to be predominant and lead to high energy.[5] The diagonal interactions are those between groups attached to $C^\alpha{}_{i-1}$ and $C^\alpha{}_{i+1}$ and which are on opposite sides of the plane defined by the skeletal bonds i, i+1. For example, in Figure 1, the interaction between R_{i-1} and R'_{i+1} or between R'_{i-1} and R_{i+1} is a diagonal interaction. Such a drastic increase in the diagonal interaction is responsible for a steep rise in the energy for displacements greater then 25°.

The pair of minima and the surrounding region of the energy surface are symmetric for the tt and gg states whereas they are unsymmetric in the tg and gt areas. The presence or absence of the symmetry depends on the type of groups taking part in the diagonal interactions. In the tt state, the diagonal interactions are $R_{i-1} \cdots (CH_3)_{i+1}$ for a (−, +) displacement in (ϕ_i, ϕ_{i+1}), and $(CH_3)_{i-1} \cdots R_{i+1}$ for a (+, −) displacement. Because of the equivalence of these interactions for (+, −) and (−, +) displacements, the energy surface and the minima are symmetric in the tt state. The case is similar for the gg state. On the other hand, the diagonally interacting groups in the gt state are $(CH_3)_{i-1} \cdots (CH_3)_{i+1}$ for a (−, +) displacement, and $(CH_2)_{i-2} \cdots R_{i+1}$ for a (+, −) shift from the perfectly staggered position (120, 0). Due to the dissimilar nature of this pair, the energy surfaces for the (+, −) and (−, +) shifts are asymmetric.

It is seen from Table III and Figure 3 that the energies of the tt and the gt states of the meso dyad are almost equal. This is contrary to the case of PMMA in which the calculations[5] showed the meso, tt state to be of lower energy than the gt state by about 1.1 kcal mol^{-1}. The difference between these

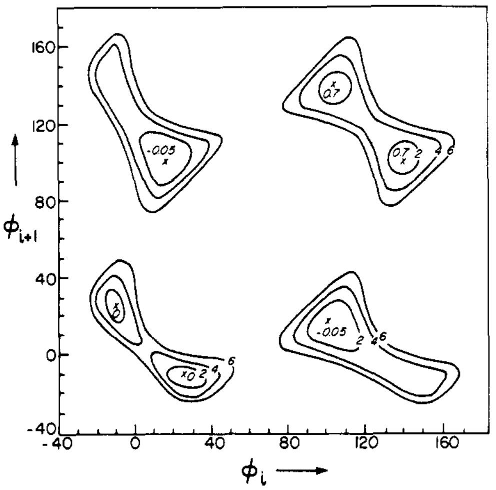

Figure 3. Energy contours at intervals of 2 kcal mol^{-1} for the meso dyad of PMS. Energies are expressed relative to the tt minimum.

Table III
Parameters Deduced from Energy Calculations for 300 K

State	z^b	$\langle E \rangle$,^{a,b} cal mol^{-1}	$\langle \phi_i, \phi_{i+1} \rangle^b$
tt, meso	8.73	0	7, 7
gt, meso	9.06	−60	105, 14
gg, meso	4.49	720	120, 120
tt, racemic	48.4	−1000	14, 14

[a] Relative to tt, meso state. [b] The values of these parameters for the gt, tg, and gg states are the same for the meso and racemic dyads.

two cases seems to be due to the larger size of the phenyl group in PMS compared to the ester side group in PMMA.

The conformational map for a racemic dyad is shown in Figure 4. The energy surface in the tt region shows a single minimum, with displacements of the same sign. The overall shapes of the surfaces in the tg, gt, and gg regions are similar to those for the meso dyad.

Since each of the "split" conformational minima are approximately symmetrically displaced from perfect staggering and since the displacements are only of the order of 20°, it is legitimate to treat each region by a single state, the ϕ_i and ϕ_{i+1} of which are averaged with respect to the energies corresponding to each region.[5,7,8] The averaging was done by calculating energies in each region, in steps of 5° in ϕ_i and ϕ_{i+1}. For each region s, the partition function z, the average energy $\langle E \rangle$, and the average rotation angles were calculated according to

$$z_s = \sum_{\phi_i} \sum_{\phi_{i+1}} \exp(-E_k/RT) \tag{2}$$

$$\langle E \rangle_s = z_s^{-1} \sum_{\phi_i} \sum_{\phi_{i+1}} E_k \exp(-E_k/RT) \tag{3}$$

$$\langle \phi_j \rangle_s = z_s^{-1} \sum_{\phi_i} \sum_{\phi_{i+1}} \phi_j \exp(-E_k/RT) \tag{4}$$

Here the subscript k refers to each conformation ϕ_i, ϕ_{i+1} and $j = i$ or $i+1$. The results are given in Table III for a temperature of 300 K. Comparing the energy maps and Table III, we find that the energies E and $\langle E \rangle$ between the states differ very little.

Statistical Weights. The high energy of the $\bar{g}$ state of the skeletal bonds eliminates the need to consider interactions of higher order. For the second-order interactions, we assign[1] a statistical weight of ω'' for the phenyl··· phenyl interaction, ω' for the phenyl··· CH_2 or CH_3 interaction, and ω for those bewteen CH_2 or CH_3 groups. The statistical weight matrix for the bond pair $i-1$, i is given by[1]

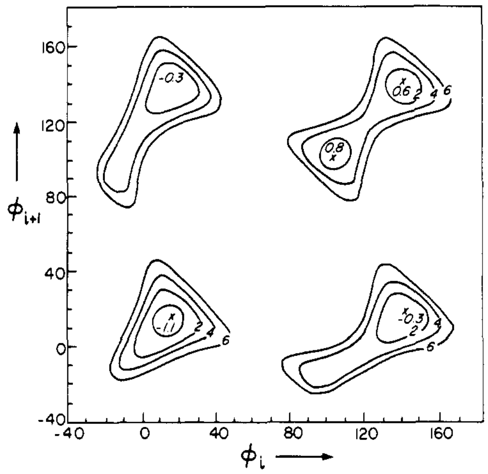

Figure 4. Energy contours at intervals of 2 kcal mol^{-1} for the racemic dyad of PMS. Energies are expressed relative to the minimum for the tt state of the meso dyad.

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{5}$$

For the bond pair i, $i+1$ in meso and racemic dyads, the matrices are respectively

$$\mathbf{U}_m'' = \begin{bmatrix} \eta^2\omega\omega'' & \eta\omega\omega' \\ \eta\omega\omega' & \omega^2 \end{bmatrix} \tag{6}$$

and

$$\mathbf{U}_r'' = \begin{bmatrix} \eta^2\omega'^2 & \eta\omega\omega' \\ \eta\omega\omega' & \omega^2 \end{bmatrix} \tag{7}$$

where η is the first-order interaction parameter for the trans state of a bond.[1] Normalizing eq 6 and 7 with respect to the tt state of the meso dyad, we obtain[5]

$$\mathbf{U}_m'' = \begin{bmatrix} 1 & \alpha \\ \alpha & \alpha^2/\beta \end{bmatrix} \tag{8}$$

and

$$\mathbf{U}_r'' = \begin{bmatrix} \beta & \alpha \\ \alpha & \alpha^2/\beta \end{bmatrix} \tag{9}$$

where

$$\alpha = \omega'/\eta\omega'' \tag{10}$$

and

$$\beta = \omega'^2/\omega\omega'' \tag{11}$$

Because of the dissimilar shapes and sizes of the energy surfaces in various states, we let[5]

$$\alpha = \alpha_0 \exp(-\langle E\alpha \rangle/RT) \tag{12}$$

$$\beta = \beta_0 \exp(-\langle E\beta \rangle/RT) \tag{13}$$

The preexponential factors determined as described previously[5] led to values of 0.6 and 0.9 for α_0 and β_0, respectively.

The calculations described here are based on a chosen set of geometrical parameters: bond lengths and bond angles. Any deviation of these parameters from the chosen values would alter the resulting energy differences between the various states, although the shapes of the contours and the preexponential factors are affected very little.[6] Hence, in the discussion which follows, only the effect of variation in the energy parameters E_α and E_β will be considered.

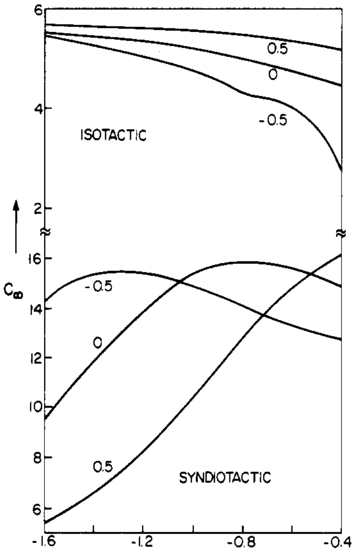

Figure 5. Characteristic ratios calculated for isotactic and syndiotactic chains for various values of E_α and E_β. The values of E_α, in kcal mol^{-1}, are marked on the curves.

Characteristic Ratios

Method of Calculation. The characteristic ratios $C_n = \langle r^2\rangle_0/nl^2$ (where n is the number of bonds in the chain and l is the length of the skeletal bond) were calculated according to the formulation which takes into account the average location of each of the states of the bond pairs in a dyad.[7] According to this method,

$$\langle r^2\rangle_0 = Z^{-1}\,\mathcal{G}_0\left(\prod_{k=1}^{x-1}\mathcal{U}'\mathcal{G}_k\right)\mathcal{G}_x \tag{14}$$

Here, Z is the configurational partition function given by

$$Z = \mathbf{U}_0\left(\prod_{k=1}^{x-1}\mathbf{U}_k'\,\mathbf{U}_k''\right)\mathbf{U}_x \tag{15}$$

and $\mathcal{U}' = \mathbf{U}'\otimes\mathbf{E}_5$ where $\mathbf{E}_5$ is the identity matrix of order five and $\otimes$ denotes the direct product of the matrices. The terminal matrices are given by

$$\mathbf{U}_0 = (1 \quad 0); \qquad \mathbf{U}_x = \begin{bmatrix}1\\1\end{bmatrix} \tag{16}$$

The product $\mathbf{U}_k'\,\mathbf{U}_k''$ refers to the kth dyad along the chain and thus reflects the stereochemical character of the dyad, either meso or racemic. The generator matrix $\mathcal{G}$ for meso and racemic dyads is given by

$$\mathcal{G}_\mathrm{m} = \begin{bmatrix}(\mathbf{G}'\mathbf{G}'')_\mathrm{tt} & \alpha(\mathbf{G}'\mathbf{G}'')_\mathrm{tg}\\ \alpha(\mathbf{G}'\mathbf{G}'')_\mathrm{gt} & (\alpha^2/\beta)(\mathbf{G}'\mathbf{G}'')_\mathrm{gg}\end{bmatrix} \tag{17}$$

and

$$\mathcal{G}_\mathrm{r} = \begin{bmatrix}\beta(\mathbf{G}'\mathbf{G}'')_\mathrm{tt} & \alpha(\mathbf{G}'\mathbf{G}'')_\mathrm{tg}\\ \alpha(\mathbf{G}'\mathbf{G}'')_\mathrm{gt} & (\alpha^2/\beta)(\mathbf{G}'\mathbf{G}'')_\mathrm{gg}\end{bmatrix} \tag{18}$$

The factors $\mathbf{G}'\mathbf{G}''$ for the respective states are calculated using the average values of the torsion angles, $\langle\phi_i\rangle$ and $\langle\phi_{i+1}\rangle$, and the matrices are of the form

$$\mathbf{G} = \begin{bmatrix}1 & 2\mathbf{l}^\mathrm{T}\mathbf{T} & l^2\\ 0 & \mathbf{T} & \mathbf{l}\\ 0 & 0 & 1\end{bmatrix} \tag{19}$$

where T is the transformation matrix,[1,4] which relates the coordinate systems of contiguous bond pairs, and $\mathbf{l}$ and $\mathbf{l}^\mathrm{T}$ are the column and row vectors of the bond. The terminal matrices are given by

$$\mathcal{G}_0 = \mathbf{U}_0\otimes\mathbf{G}_1 \tag{20}$$

and

$$\mathcal{G}_x = \mathbf{U}_x\otimes\mathbf{G}_x \tag{21}$$

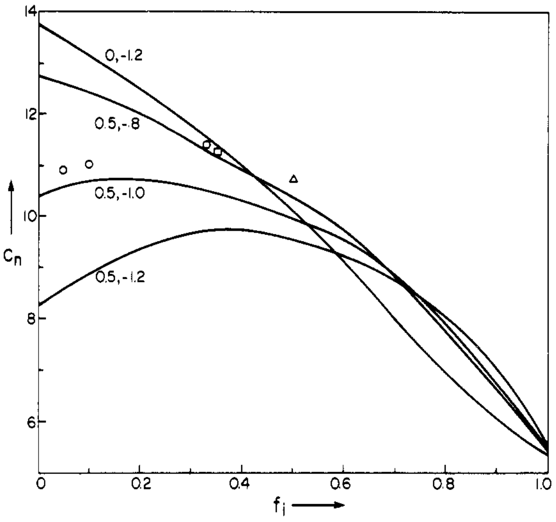

Figure 6. Characteristic ratios calculated for stereoirregular chains of various isotacticity. The values of E_α and E_β, in that order, in kcal mol^{-1}, are marked on the curves. The experimental values of Cowie and Bywater[12] (○), Cowie et al.,[13] (□) and Noda et al.[14] (△) are shown.

Stereoregular Chains. The characteristic ratio C_∞ calculated for isotactic and syndiotactic chains with various values for E_α and E_β is given in Figure 5. For the isotactic chain, the values of C_∞ decrease as E_β increases, although it is not pronounced. The gg state of the meso dyad depends inversely on β. As the value of E_β increases (the parameter β decreases), the population of the gg state is increased resulting in a lower value of C_∞. The curves also show that the values of C_∞ increase with an increase in E_α, in the range of E_α shown here. An increase in α leads to interspersion of more gauche states and hence the characteristic ratio decreases. The effect is more pronounced when the value of β decreases resulting in an increase in the gg population.

For the syndiotactic chain, the effect of E_β on C_∞ is significant. With $E_\alpha = 0.5$, C_∞ is very small for E_β, -1.6 kcal mol^{-1} and an increase in E_β increases the value of C_∞ throughout the range given here. When E_β is low, the population of the tt state is high. Since the bond angles $\mathrm{C^\alpha CC^\alpha}$ and $\mathrm{CC^\alpha C}$ along the backbone differ by 12°, a perpetuation of tt state would lead to a polygonal form for the chain,[5] resulting in a small value for C_∞. With a decrease in β, the tt population is decreased relative to the gt states and the latter serve to disrupt the polygonal formation and increase C_∞. It is also seen that up to a certain value of E_β, an increase in α increases the gauche population and hence the C_∞.

Curves for $E_\alpha = -0.5$ and $E_\alpha = 0$ kcal mol^{-1} show an increase in C_∞ with an increase in E_β up to a certain value of E_β and then show a decrease in C_∞. The maximum is at $E_\beta = -1.2$ with $E_\alpha = -0.5$ and at $E_\beta = -0.8$ with $E_\alpha = 0$. The combined effect of an increase in α and a decrease in β serves to increase the population of gg states and this results in a decrease in C_∞ in these cases.

Stereoirregular Chains. The characteristic ratios were calculated for Monte Carlo chains of 200 units each, as a function of f_i, the fraction of meso dyads in the chain.[5,11] The calculations were performed at intervals of 0.2 in f_i. Averages of the characteristic ratios C_n for 10 chains for each f_i and the standard deviations are shown in Figure 6, for a few values of

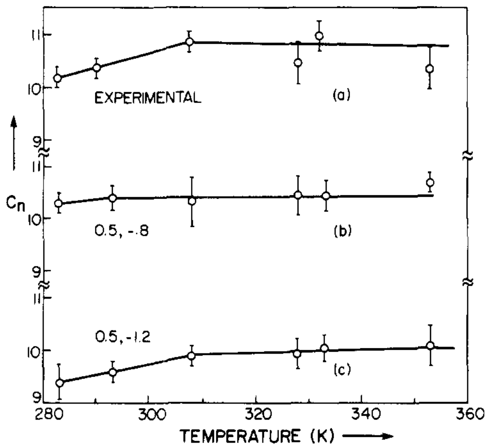

Figure 7. Experimental[14] (a) and calculated (b and c) values of C_n, as a function of temperature. The values of E_α and E_β, in that order, in kcal mol^{-1}, are given in (b) and (c).

E_α and E_β. The value of $f_i = 1$ corresponds to a purely isotactic chain and $f_i = 0$ refers to the syndiotactic chain.

Variations in C_n due to changes in the parameters are more pronounced in the regions of $f_i \approx 0$. This effect decreases as f_i approaches a value of about 0.5 and thereafter, as the chain assumes predominently isotactic character, the variations are small. This is in keeping with the results shown in Figure 5. The experimental data[12–14] on the characteristic ratios are also marked in Figure 6. The value of f_i in each case was taken as quoted by the authors of the experimental work. It is seen that values of $E_\alpha \approx 0.5$ and $E_\beta \approx -1.0$ kcal mol^{-1} reproduce the experimental results satisfactorily. These energy parameters are close to those deduced from the present calculations.

The effect of temperature on $\langle r^2 \rangle_0$ of PMS was investigated by Noda et al.,[14] using theta and apparent theta solvents. They found that the value of K_Θ increases in the range of 10 to 35 °C, and thereafter the effect is insignificant. The values of C_n, calculated for different temperatures, for an atactic chain with $f_i = 0.5$, are given in Figure 7. Two sets of values of E_α and E_β were used. The values of C_n, calculated from the experimental K_Θ values of Noda et al., are also given in this figure. It is seen that the calculated temperature dependence parallels that of the experimental results. Slight differences in the experimental and theoretical values of C_n may be due to the lack of precise information on the value of f_i for the polymer employed in the experimental work. This fact has been discussed by Noda et al.[14]

Acknowledgments. The author thanks Dr. M. L. Hair of this center for his interest in this work and the encouragement he provided.

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Biphenylene as Cross-Linking Sites for Polyquinolines

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Received December 14, 1976

ABSTRACT: Biphenylene units were incorporated into polyquinolines in order to provide a site which could enter into a thermal cross-linking reaction above 300 °C. The cross-linking reaction takes place thermally via a radical ring opened intermediate without the evolution of volatiles to afford thermally stable cross-links. The incorporation was accomplished by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4′-diacetyldiphenyl ether with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether in the synthesis of the polyquinoline. Lower curing temperatures and shorter curing times were possible in the presence of rhodium catalysts.

Since the strained biphenylene ring is known to open thermally at 375–400 °C giving dimeric or polymeric products, probably via a diradical intermediate,[1,2] biphenylene units incorporated into a macromolecular backbone could serve as cross-linking sites for high-temperature polymers. Such a cross-linking mode would be especially attractive because no volatile material is produced and the resulting cross-link would be thermally stable.

Recent work in this laboratory has shown that the Friedlander condensation of suitable bisaminoketones with ketomethylene monomers affords high molecular weight polyquinolines.[3,4] Thus, the introduction of biphenylene (**1**) into a polyquinoline backbone by polycondensation of an aminoketone monomer with the readily available 2,6-diacetylbiphenylene[5,6] (**2**) appeared to be feasible. In the present study, the thermal behavior and the cross-linking reaction of a homopolymer of **2** with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**5**) and two copolymers containing **2** with variable amounts of 4,4′-diacetyldiphenyl ether (**6**) have been explored.