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# Thermoelastic and Strain-Birefringence Studies on Poly(methylphenylsiloxane) Networks

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ABSTRACT: A sample of poly(methylphenylsiloxane) of known stereochemical structure was cross-linked by means of dicumyl peroxide. The resulting elastomeric networks were studied in elongation, in both the unswollen and swollen states, over the temperature range 10–70 °C. The most important experimental results obtained were values of the strain birefringence, which was found to be negative. Theoretical calculations based on rotational isomeric state theory were carried out to interpret the temperature coefficient of the unperturbed dimensions, $\mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T$, the optical-configuration parameter, $\Delta a$, and its temperature coefficient. The agreement between theory and experiment was excellent, suggesting that intermolecular correlations, which are usually considered to be responsible for a large discrepancy between experimental and theoretical values of the stress optical properties, are very small in this polymer. Contrary to other systems, swelling the networks with decalin worsens this agreement.

## Introduction

Among the configurational properties of polymeric materials, the temperature coefficient of the unperturbed dimensions, $\mathrm{d} \ln \langle r^2 \rangle_0/\mathrm{d}T$, and the birefrigence, $\Delta n$, are the ones most extensively studied in elastomeric networks.[1,2] They can provide valuable information on the molecular characteristics of the chains from which the networks are constituted. The temperature coefficient of the unperturbed dimensions can be obtained from stress–temperature (thermoelastic) experiments. This technique has been proven to be very useful to obtain reliable data on many elastomeric systems.[1] The birefringence is an optical property from which one can obtain the stress–optical coefficient, $C$, the related optical-configuration parameter, $\Delta a$, and its temperature coefficient.

All these quantities can be evaluated theoretically from structural and configurational parameters of the polymer chains by means of the rotational isomeric state theory.[3] However, in the case of the strain-birefringence studies, poor agreement has been found between theory and experiment, particularly in the case of symmetric chains. Few studies have been performed on asymmetric chains,[4-6] in which the birefringence is usually negative, and, in this case, the agreement seems to be much better.[4,5] Another important feature of these chains is that their configurational properties usually show a strong dependence on the stereochemical structure. Therefore, it would be interesting to carry out more studies on these types of polymers, including asymmetric chains.

Poly(methylphenylsiloxane) (PMPS) is an important inorganic polymer, and the above studies would provide information about its conformation. The presence of a bulky and anisotropic side group in the chain makes the birefringence negative in the oriented polymer. Also, the special characteristics of the siloxane backbone confer very interesting properties to these chains. The inequality of the two skeletal bond angles and the long O–Si bond make the interaction between two phenyl groups, situated on the same side of the chain, attractive. This is contrary to the situation found in vinyl chains (for instance, polystyrene), in which this same interaction is repulsive.[7]

The dependence of some configurational properties of PMPS on the stereochemical structure has been studied theoretically by Mark and Ko.[8] Their calculations included the characteristic ratio and the temperature coefficient of the unperturbed dimensions. The required conformational energies were obtained from semiempirical interatomic potential energy functions and from known results on poly(dimethylsiloxane). Unfortunately, there are only a few experimental results to compare with the calculated values, and even those were obtained in polymer samples of unknown stereochemical structure.[9,10] Therefore, only a tentative comparison could be made.

The purpose of the present investigation is twofold: on the one hand, to provide more information on the configurational-dependent properties of asymmetric chains, particularly in the case of the optical properties, and on the other hand, to apply the rotational isomeric state

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**Table I**
**Characteristics and Elastic Parameters of the PMPS Networks**

| network | DCP wt % | sol fraction wt % | $T$, °C | $[f_{ph}^*]^a$ | $10^{-4}M_c^b$ |
|---|---|---|---|---|---|
| A | 4.2 | 12.1 | 25 | 0.0287 | 4.4 |
| B | 4.8 | 11.3 | 10 | 0.0335 | 3.8 |
| | | | 25 | 0.0309 | 4.2 |
| | | | 40 | 0.0336 | 3.5 |

[a] Reduced force in the phantom limit, in N mm$^{-2}$. [b] Molecular weight between cross-links.

theory to study the conformational properties of PMPS chains using a stereochemically well-characterized polymer sample.

## Experimental Section

**Materials.** The poly(methylphenylsiloxane) sample was kindly provided by Dr. J. R. Falender from Dow Corning Co. (Midland, MI). The polymer was purified by precipitation with methanol from a toluene solution. The molecular weight was measured by light scattering using a Fica 42000 photogoniodiffusometer. A value of $M_w = 3.24 \times 10^5$ was found . The sample was characterized with regard to its stereochemical structure by high-resolution $^1$H NMR spectroscopy. The spectra were obtained at room temperature on a Bruker WM-360, working at 360 MHz in the FT mode. Deuterated chloroform was used as solvent and reference.

The solvent used for the swollen networks was reagent-grade decalin (Carlo Erba). It was chosen because it is a good solvent for the polymer and has low volatility. Its density ($\rho_d = 0.896$ g/cm$^3$ at 20 °C) and index of refraction ($n = 1.4832 - 4.714 \times 10^{-4}T$, with $T$ in ° C) were taken from the literature.[11,12]

**Preparation of the Networks.** Two networks were prepared by cross-linking the high molecular weight polymer with dicumyl peroxide (DCP). The polymer and peroxide were dissolved in a small amount of chloroform to get a uniform mixing of both ingredients. After the solvent was removed under vacuum at room temperature, the samples were cured in Teflon molds in a small press at 150 °C for 16 h. The resulting networks were then extracted with toluene. The characteristics of the networks thus prepared are given in Table I. The refractive index of network B was measured as a function of temperature in an Abbe refractometer (Atago, Model 1.111) in the range 10–50 °C. The index of refraction was found to be given by $n = 1.5626 - 3.54 \times 10^{-4}T$ (with $T$ in °C). The density was measured by pycnometry and found to be $\rho_p = 1.115$ g/cm$^3$ at 25 °C.

**Apparatus.** Stress birefringence–strain experiments were carried out in the usual manner.[12,13] Briefly, the light source was a 2-mW, 632.8-nm He–Ne laser (Ealing, Model 25-0837) and the polarizer and analyzer were Glan-Thompson prisms (Ealing, 34-5215). The retardation was measured with a quarter-wave plate (Ealing, 34-5736) placed between the network and the analyzer. This last component is mounted in a rotary stage (Ealing, 22-8197) which allows measurement of its rotation to a precision of 5′ of arc. A photodiode was used as the light detector. The optical bench and other accessories were obtained from Ealing Corp.

The glass sample cell had a double-wall jacket, thus permitting temperature control by circulation of water through those parts of the cell not in the path of the laser beam. The temperature was measured with a digital thermometer whose probe was maintained close to the sample. The elastic forces were measured with a "strain" gauge (Gould UC-3), whose signal was monitored with a recorder, and the deformation was measured with a cathetometer (Ealing, 11-5402).

**Mechanical and Optical Measurements.** Most of the experiments were carried out at constant length. In the case of the unswollen samples, the network strip being studied was mounted between two clamps, the lower one fixed and the upper one attached to the strain gauge, which can be moved up and down so as to impose the required deformation. The sample was extended to the desired elongation, $\alpha = L/L_0$, and kept overnight at the highest temperature studied. The temperature was then decreased in several steps, and the force and birefringence were recorded when they became constant. After the lowest temperature of measurement was reached, the temperature was increased again to check the reversibility of the experiments. In the case of the swollen networks, it was more convenient to reverse the procedure by beginning the measurements at the lowest temperature in order to minimize the evaporation of the solvent.

Also a few experiments were carried out at constant temperature by varying the length of the samples.

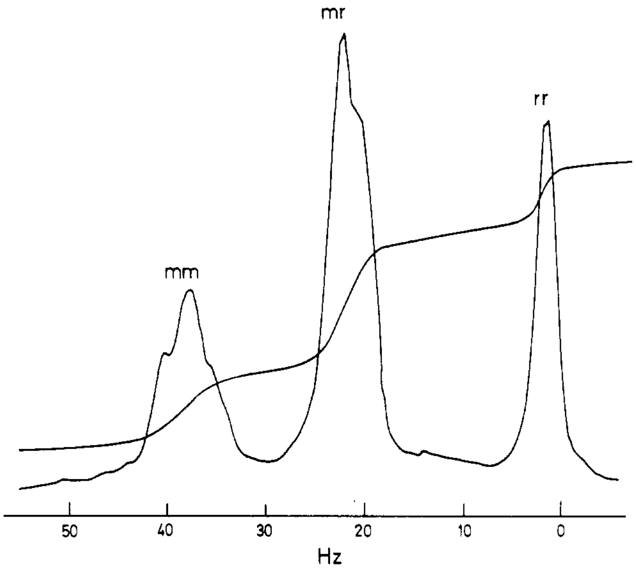

**Figure 1.** $^1$H NMR signal corresponding to the $\alpha$-methyl protons of the PMPS chain.

## Experimental Results

**NMR Results.** $^1$H NMR spectra of PMPS show two bands at $\delta \simeq 7$, corresponding to phenyl protons, and $\delta \simeq 0$, corresponding to $\alpha$-methyl protons. This second band is clearly resolved into three peaks (Figure 1), which have been assigned to isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads by analogy with $\alpha,\alpha'$-disubstituted vinylic polymers with $\alpha$-methyl groups.[14] From the integral of such peaks, the percent of each kind of triads has been obtained as $W_{mm} = 27\%$, $W_{mr} = 49\%$, and $W_{rr} = 24\%$. The percentage of meso ($W_m$) and racemic ($W_r$) diads has been calculated from those numbers as

$$W_m = (1/2)(2W_{mm} + W_{mr}) \qquad (1)$$

$$W_r = (1/2)(2W_{rr} + W_{mr}) \qquad (2)$$

and the results give 51% and 49% meso and racemic diads, respectively.

The average lengths of the meso and racemic sequences ($l_m$ and $l_r$) are calculated from

$$l_m = (2W_{mm} + W_{mr})/W_{mr} \qquad (3)$$

$$l_r = (2W_{rr} + W_{mr})/W_{mr} \qquad (4)$$

which gives 2.1 for $l_m$ and 2.0 for $l_r$.

The persistence ratio ($\rho$), calculated as

$$\rho = l_m W_r = l_r W_m \qquad (5)$$

equals 1.00, and therefore, the chain configuration follows a Bernoullian statistics. That means the distribution of m and r diads along the chain is random. Besides, since m $\simeq$ r $\simeq$ 0.5, the polymer is ideal-like because the probability of finding an m or r diad after a given one is the same, and therefore, m or r sequences are not longer than 2.

When using Bernoullian statistics, it is possible to calculate the contribution of any sequence, knowing the percentage of diads. From now on, the tacticity will be therefore expressed as a function of diad content ($W_m$ =

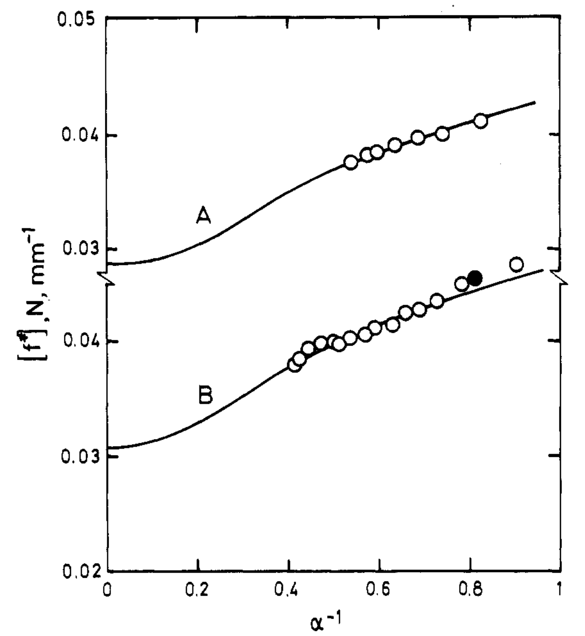

**Figure 2.** Stress–strain isotherms of the two PMPS networks obtained at 25 °C.

0.50) because it has the advantage of using only one parameter.

**Elastic and Thermoelastic Results.** In order to determine the degree of cross-linking in the networks prepared, stress–strain isotherms were carried out at several temperatures. The results were treated in terms of the "reduced stress", or modulus, defined as[15]

$$[f^*] = f/[A^*(\alpha - \alpha^{-2})] \tag{6}$$

where $f$ is the elastic force at equilibrium and $A^*$ is the cross-sectional area of the unstretched sample. The reduced stress was interpreted by means of the recent molecular theory of Flory,[16,17] according to which

$$[f^*] = [f_{ph}^*](1 + f_c/f_{ph}) \tag{7}$$

where $f_c$ is the contribution to the force from the constraints on the junction fluctuations and $f_{ph}$ is the force that would be exerted by the phantom network. Thus, $[f_{ph}^*]$ is the reduced force in the limit of high extension in which the ratio $f_c/f_{ph}$ vanishes. The factor multiplying $[f_{ph}^*]$ is given in terms of two parameters $\kappa$ and $\zeta$ that specify respectively the constraints on cross-link fluctuations and the dependence of these fluctuations on strain.[16]

All the isotherms were fitted with $\kappa = 5.0$ and $\zeta = 0.00$, and some of them are shown in Figure 2. The values of $[f_{ph}^*]$ obtained are listed in Table I. From these values and assuming perfect tetrafunctional networks, we can estimate the molecular weight between cross-links, $M_c$, according to the equation

$$[f_{ph}^*] = (1/2)\rho_p RTM_c^{-1} \tag{8}$$

where $\rho_p$ is the density of the network. Values of $M_c$ thus calculated are given in the last column of Table I. The cross-link densities of networks A and B were found to be very similar, the molecular weights between cross-links being 44 000 and 38 000, respectively.

The force–temperature, thermoelastic data were interpreted in the usual manner in terms of ln $(f^*/T)$ as a function of temperature. Some typical results are plotted in Figure 3. The data are linear over the whole range of temperatures studied, and also, they show complete reversibility. The experimental points were fitted by least-squares analysis. The information that can be obtained from this type of data is the fraction $f_e/f$ of the force that is energetic in origin and the temperature coefficient d ln $\langle r^2\rangle_0/dT$ of the unperturbed dimensions.[3] These quantities can be calculated from the slopes of the experimental results by using the standard equations[18]

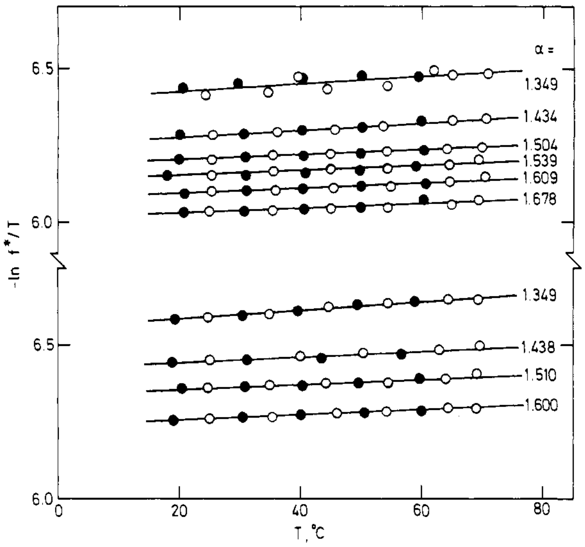

**Figure 3.** Thermoelastic results for the unswollen B network. The open and filled symbols show results obtained upon decreasing and increasing temperature, respectively. Each line is labeled with the value of the elongation at 25 °C. $f^*$ units are kg/cm$^2$.

**Table II**
**Thermoelastic Results**[a]

| network | $\alpha$[b] | $f_e/f$[c] | $10^3$(d ln $\langle r^2\rangle_0$/d$T$)[d] |
|---|---|---|---|
| A | 1.149 | 0.22 | 0.70 |
| | 1.367 | 0.27 | 0.85 |
| | 1.577 | 0.24 | 0.74 |
| B | 1.349 | 0.21 | 0.66 |
| | 1.349 | 0.27 | 0.84 |
| | 1.434 | 0.26 | 0.82 |
| | 1.438 | 0.17 | 0.52 |
| | 1.504 | 0.16 | 0.49 |
| | 1.510 | 0.16 | 0.51 |
| | 1.539 | 0.17 | 0.54 |
| | 1.600 | 0.17 | 0.53 |
| | 1.609 | 0.18 | 0.57 |
| | 1.678 | 0.17 | 0.54 |
| | | 0.20 ± 0.04[e] | 0.64 ± 0.13[e] |

[a] Temperature range 20–70 °C. [b] Elongation ratio. [c] Fraction of the force that is energetic in origin. [d] Temperature coefficient of the unperturbed dimensions. [e] Average value.

$$f_e/f = T(\text{d ln}\,\langle r^2\rangle_0/\text{d}T) = -T[\partial \ln (f^*/T)/\partial T]_{p,l} - \beta T/(\alpha^3 - 1) \tag{9}$$

where $\beta$ is the thermal expansion coefficient of the sample whose value was taken to be[9] $\beta = 8.52 \times 10^{-4}$ deg$^{-1}$. All the values thus obtained are given in Table II. They give an average value of d ln $\langle r^2\rangle_0$/d$T$ = (0.64 ± 0.13) × $10^{-3}$ deg$^{-1}$, in very good agreement with a previous result obtained on an other stereochemically uncharacterized PMPS sample.[9]

**Birefringence Results.** A few experiments were carried out at constant temperature to see the dependence of the birefringence, $\Delta n$, on stress. The results are plotted in Figure 4, in which the birefringence is shown as a function of the true stress, $f/A$, where $A$ is the cross-sectional area of the stretched sample. From the slopes of the straight lines we can obtain the stress-optical coefficient $C = \Delta n/(f/A)$, which is almost independent of the

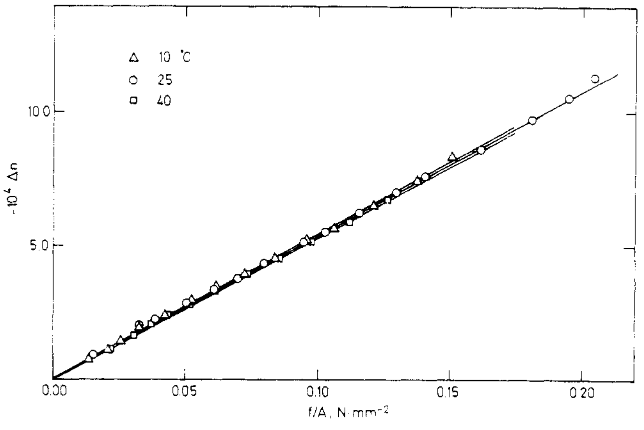

**Figure 4.** Dependence of the birefringence on the true stress at several temperatures for network B. The slope of each line is the stress-optical coefficient $C$.

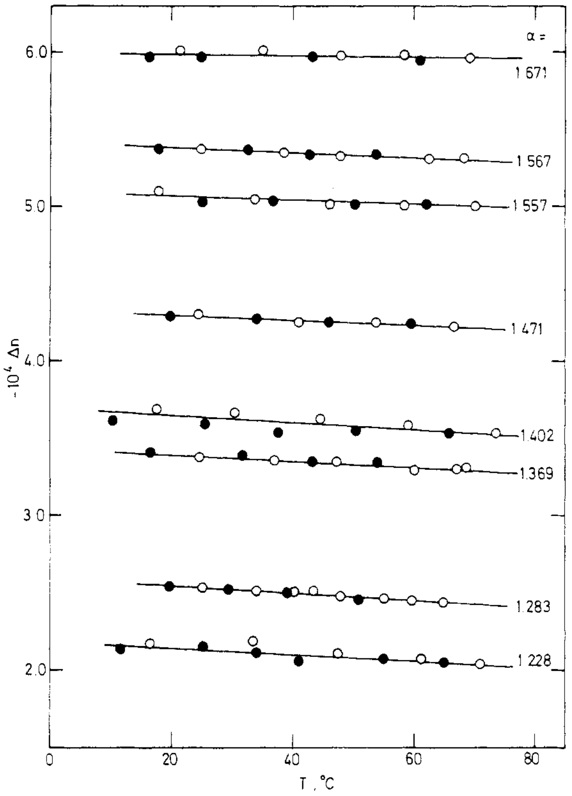

**Figure 5.** Birefringence results for the unswollen B network as a function of temperature (see legend to Figure 3.)

temperature. The values of $-10^3C$ (in mm$^2$ N$^{-1}$) are 5.73 at 25 °C for network A and 5.42, 5.38, and 5.31 at 10, 25, and 40 °C, respectively, for network B.

More interesting results are those measured at constant sample length by varying the temperature. Typical results, obtained on network B, are shown in Figure 5. As can be seen, the data are linear and highly reversible. These results were used to calculate values of the optical-configuration parameter, defined by[20,21]

$$\Delta a = \frac{45kTC}{2\pi}\,\frac{n}{(n^2+2)^2} \tag{10}$$

where $k$ is the Boltzmann constant and $n$ the refractive index of the network. In the case of swollen samples, $n$ was taken as the weighted average value of the polymer and the diluent at the corresponding degree of swelling.

**Table III**
**Birefringence Results**

| network | $\alpha$[a] | $10^7 \times$ $(\mathrm{d}\Delta n/\mathrm{d}T)$,[b] deg$^{-1}$ | $-10^{26} \times$ $(\mathrm{d}\Delta a/\mathrm{d}T)$,[c] cm$^3$ deg$^{-1}$ |
|---|---|---|---|
| A | 1.149 | 1.44 | 1.54 |
|  | 1.367 | 1.51 | 1.07 |
|  | 1.577 | 1.38 | 1.25 |
| B | 1.228 | 2.13 | 3.64 |
|  | 1.283 | 2.46 | 3.01 |
|  | 1.369 | 2.06 | 2.32 |
|  | 1.402 | 2.26 | 3.78 |
|  | 1.471 | 1.51 | 2.35 |
|  | 1.557 | 1.28 | 3.66 |
|  | 1.567 | 1.51 | 2.30 |
|  | 1.671 | (0.39) | 1.89 |
|  |  | 1.75 ± 0.40[d] | 2.44 ± 0.93[d] |

[a] Elongation ratio. [b] Temperature coefficient of the strain birefringence. [c] Temperature coefficient of the optical-configuration parameter. [d] Average value.

**Table IV**
**Birefringence Results for Swollen Samples**

| $v_2$[a] | $-10^{24}\Delta a$,[b] cm$^3$ | $-10^{26}(\mathrm{d}\Delta a/\mathrm{d}T)$,[c] cm$^3$ deg$^{-1}$ |
|---|---|---|
| 1.000 | 12.1 | 2.44 |
| 0.673 | 11.5 | 0.73 |
| 0.488 | 9.12 | 1.18 |
| 0.350 | 8.32 | 0.71 |
| 0.211 | 8.10 | 1.12 |
| 0.204 | 8.50 | 1.69 |

[a] Volume fraction of polymer. [b] Optical-configuration parameter at 25 °C. [c] Temperature coefficient of the optical-configuration parameter.

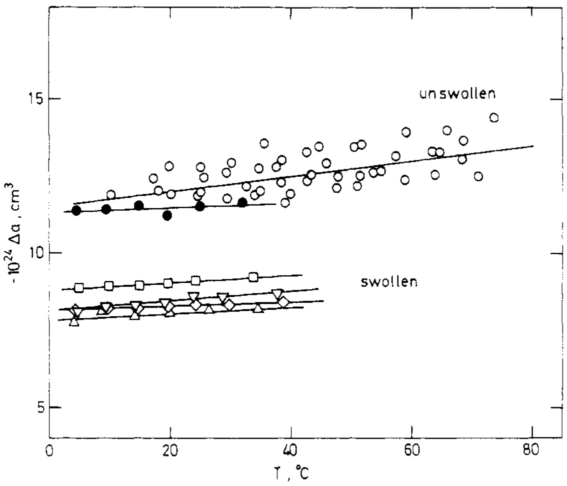

**Figure 6.** Comparison among the optical-configuration parameters for the swollen and unswollen B network. (○) Representative results obtained on the unswollen network. Swollen samples: (●) $v_2$ = 0.673; (□) $v_2$ = 0.488; (▽) $v_2$ = 0.350; (◇) $v_2$ = 0.211; (△) $v_2$ = 0.204.

In the study of the configurational-dependent properties not only is the absolute value of the property important but the temperature dependence is also of great interest. For this reason, values of the temperature coefficients of $\Delta n$ and $\Delta a$ are separately presented in Table III for the unswollen samples. The average values of the optical-configuration parameter, $-10^{24}\Delta a$, at 25 and 50 °C are respectively 12.1 ± 0.5 and 12.7 ± 0.6 cm$^3$. Representative results of both swollen and unswollen networks are shown in Figure 6, and the numerical results obtained on swollen samples are given in Table IV. As can be seen, swelling of the networks reduces the absolute value of the optical-configuration parameter from $12.1 \times 10^{-24}$ to $8.5 \times 10^{-24}$ cm$^3$ at $v_2$ = 0.204 and 25 °C. The temperature coefficient is also reduced by swelling to about half the value corresponding to the unswollen networks.

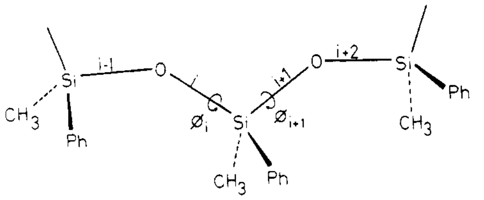

**Figure 7.** A segment of the isotactic PMPS chain shown in its planar all-trans conformation.

**Table V**
**Summary of Energy Parameters (in kcal/mol)**

$E_\sigma = 0.35$ $\quad E_{\omega''} = -0.90$
$E_\omega = 1.60$ $\quad E_{\omega'''} = -0.50$
$E_{\omega'} = -2.50$ $\quad E_\delta = -1.00$

## Theoretical Calculations

**Geometry.** Figure 7 shows a segment of the isotactic PMPS chain in its planar all-trans conformation. The geometrical data used for the present calculations were taken from ref 8. The parameters used were bond lengths of 1.64 and 1.90 Å for bonds Si–O and Si–C, respectively. Values of 143 and 109.5° were used for the valence angles between bonds meeting at the O and Si atoms, respectively. Rotational isomers were placed at $\phi = 0$ and $\pm 120°$.

**Energy Parameters and Statistical Weight Matrices.** Energetic parameters were also taken from ref 8 and are summarized in Table V. Statistical weight matrices of ref 8 were converted into their equivalent according to the scheme described in ref 22. Thus, $\mathbf{U}'$ matrices representing a pair of bonds flanking a Si atom (like $i$, $i + 1$ in Figure 7) are

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

$\mathbf{U}''$ matrices that represent bonds flanking an O atom are

$$\mathbf{U}''_{\mathrm{m}} = \begin{bmatrix} \omega'\omega''' & \sigma\omega'' & \sigma\delta\omega'' \\ \omega'' & \sigma\omega\omega''' & \sigma\delta \\ \omega''\delta & \sigma\delta & \sigma\omega\omega' \end{bmatrix}$$

$$\mathbf{U}''_{\mathrm{r}} = \begin{bmatrix} (\omega'')^2 & \sigma\delta\omega''' & \sigma\omega' \\ \delta\omega''' & \sigma & \sigma\omega\omega'' \\ \omega' & \sigma\omega\omega'' & \sigma\delta^2 \end{bmatrix}$$

These matrices can be easily obtained from $\mathbf{U}_{\mathrm{d}}$, $\mathbf{U}_{\mathrm{dd}}$, and $\mathbf{U}_{\mathrm{dl}}$ matrices used in ref 8. In fact, $\mathbf{U}''_{\mathrm{r}}$ is identical with $\mathbf{U}_{\mathrm{dl}}$, whereas $\mathbf{U}'$ and $\mathbf{U}''_{\mathrm{m}}$ are obtained by interchanging columns 2 and 3 of $\mathbf{U}_{\mathrm{d}}$ and $\mathbf{U}_{\mathrm{dd}}$, respectively.

**Anisotropic Part of the Polarizability Tensors.** We represent by $\hat{\alpha}_i$ the contribution to the anisotropic part of the polarizability tensor of the chain, $\hat{\alpha}$, due to bond $i$ (joining skeletal atoms $i - 1$ and $i$) and the group attached to skeletal atom $i - 1$. On this basis two different contributions are needed:

$$\hat{\alpha}_i = \hat{\alpha}_{\mathrm{OSi}} \qquad \hat{\alpha}_{i+1} = \hat{\alpha}_{\mathrm{OSi}} + \mathbf{T}\hat{\alpha}_{\mathrm{SiPh}}\mathbf{T}^{\mathrm{T}} + \mathbf{T}'\hat{\alpha}_{\mathrm{SiCH_3}}\mathbf{T}'^{\mathrm{T}} \quad (11)$$

where $\mathbf{T}$ and $\mathbf{T}'$ represent the transformation matrices required to bring the coordinate systems attached to the Si–Ph and Si–CH$_3$ bonds, respectively, into coincidence with the reference frame associated with skeletal bond $i + 1$ and are fully described elsewhere.[23]

The $\hat{\alpha}_i$ tensor has the form (referred to a coordinate system having the $x$ axis along the Si–O bond)

$$\hat{\alpha}_i = \Delta\alpha_{\mathrm{SiO}}\mathbf{J} \quad (12)$$

where $\mathbf{J} = \mathrm{diag}\,(^2/_3, -^1/_3, -^1/_3)$ and $\Delta\alpha_{\mathrm{SiO}}$ represents the difference between the polarizability along the $x$ axis (direction of the bond) and the mean of polarizabilities along the $y$ and $z$ axes. From the analysis of the stress-optical behavior of poly(dimethylsiloxane), Flory and coworkers[20] obtained $\Gamma_{\mathrm{PDMS}} = \Delta\alpha_{\mathrm{SiO}} - \Delta\alpha_{\mathrm{SiC}} + \Delta\alpha_{\mathrm{CH}} = 0.047 \times 10^{-24}$ cm$^3$; this result, together with the literature values[24,25] of $\Delta\alpha_{\mathrm{CH}} = 0.21 \times 10^{-24}$ cm$^3$ and $\Delta\alpha_{\mathrm{SiC}} = 1.46 \times 10^{-24}$ cm$^3$, allows the evaluation of $\Delta\alpha_{\mathrm{SiO}} = 1.3 \times 10^{-24}$ cm$^3$.

$\hat{\alpha}_{\mathrm{SiPh}}$ can be expressed as

$$\hat{\alpha}_{\mathrm{SiPh}} = \Delta\alpha_{\mathrm{Siph}}\mathbf{J} + \Delta\alpha^{+}{}_{\mathrm{SiPh}}\mathbf{J}^{+} \quad (13)$$

in a coordinate system having the $x$ axis along the Si–Ph bond and the $z$ axis in the plane of the aromatic ring; $\mathbf{J}^{+} = \mathrm{diag}\,(0, -^1/_2, -^1/_2)$ and $\Delta\alpha^{+}{}_{\mathrm{SiPh}}$ represent the difference in polarizabilities along the $y$ and $z$ axes. The group SiPh may be formally obtained by substitution of one CH bond of a molecule of benzene by a Si–C bond; therefore, the parameters $\Delta\alpha_{\mathrm{SiPh}}$ and $\Delta\alpha^{+}{}_{\mathrm{SiPh}}$ can be evaluated as

$$\Delta\alpha_{\mathrm{SiPh}} = \Delta\alpha_{\mathrm{B}} + \Delta\alpha_{\mathrm{CSi}} - \Delta\alpha_{\mathrm{CH}} \quad (14)$$

$$\Delta\alpha^{+}{}_{\mathrm{SiPh}} = \Delta\alpha^{+}{}_{\mathrm{B}} + \Delta\alpha^{+}{}_{\mathrm{CSi}} - \Delta\alpha_{\mathrm{CH}} = \Delta\alpha^{+}{}_{\mathrm{B}} \quad (15)$$

since $\Delta\alpha^{+}{}_{\mathrm{SiC}} = \Delta\alpha^{+}{}_{\mathrm{CH}} = 0$ owing to the cylindrical symmetry of any single bond. The parameters $\Delta\alpha_{\mathrm{B}}$ and $\Delta\alpha^{+}{}_{\mathrm{B}}$ were reported by Flory and co-workers[23,26] as 3.85 and −3.0, respectively, both in units of $10^{-24}$ cm$^3$; from these values and those above for $\Delta\alpha_{\mathrm{CSi}}$ and $\Delta\alpha_{\mathrm{CH}}$, we obtained $\Delta\alpha_{\mathrm{SiPh}} = 5.10$ and $\Delta\alpha^{+}{}_{\mathrm{SiPh}} = -3.0$, both in units of $10^{-24}$ cm$^3$.

In a similar fashion, if we use a coordinate system having the $x$ axis along the SiCH$_3$ bond, we can write

$$\hat{\alpha}_{\mathrm{SiCH_3}} = \Delta\alpha_{\mathrm{SiCH_3}}\mathbf{J} \quad (16)$$

and if we assume tetrahedral symmetry for the CH$_3$ group

$$\Delta\alpha_{\mathrm{SiCH_3}} = \Delta\alpha_{\mathrm{SiC}} + \Delta\alpha_{\mathrm{CH_3}} = \Delta\alpha_{\mathrm{SiC}} - \Delta\alpha_{\mathrm{CH}} \quad (17)$$

With the literature values[24,25] of $\Delta\alpha_{\mathrm{SiC}}$ and $\Delta\alpha_{\mathrm{CH}}$, we obtained $\Delta\alpha_{\mathrm{SiCH_3}} = 1.25 \times 10^{-24}$ cm$^3$.

Substitution of the numerical values of all the optical parameters together with the $\mathbf{T}$ and $\mathbf{T}'$ matrices[23] and the geometry described above for the PMPS chain yields

$$\hat{\alpha}_i = \mathrm{diag}\,(0.866, -0.433, -0.433) \quad (18)$$

$$\hat{\alpha}_{i+1} = \begin{bmatrix} -1.213 & -2.175 & 0.639 \\ -2.175 & -0.972 & -0.905 \\ 0.639 & -0.905 & 2.185 \end{bmatrix} \quad (19)$$

both in units of $10^{-24}$ cm$^3$.

**Results.** The optical-configuration parameter was calculated as[3,20,21,27]

$$\Delta a = (3/2)\langle r^{\mathrm{T}}\hat{\alpha}r\rangle_0/\langle r^2\rangle_0 \quad (20)$$

Standard methods of matrix multiplication[3,27] were used to calculate values of $\Delta a$ for different degrees of polymerization $x$ up to $x = 100$. Asymptotic limits of $\Delta a$ as a function of $x$ were reached for $x \simeq 60$ (differences between values of $\Delta a$ calculated for $x = 60$ and $x = 100$ are ca. 1–2%). All the values reported below were calculated for $x = 100$. Monte Carlo simulations with Bernoullian placements of meso and racemic diads were used to generate chains with each desired fraction of meso diads, $W_{\mathrm{m}}$. Results reported below for $0 < W_{\mathrm{m}} < 1$ are averages over 20 chains.

Figure 8 shows the dependence of $\Delta a$ on the fraction of meso diads $W_{\mathrm{m}}$, and Table VI summarizes the variations of $\Delta a$ with the temperature, conformational energies, and the optical parameters used in the calculations.

## Discussion

As can be seen in Figure 8, the calculated values of $\Delta a$ are negative for any value of $W_{\mathrm{m}}$. The same behavior is

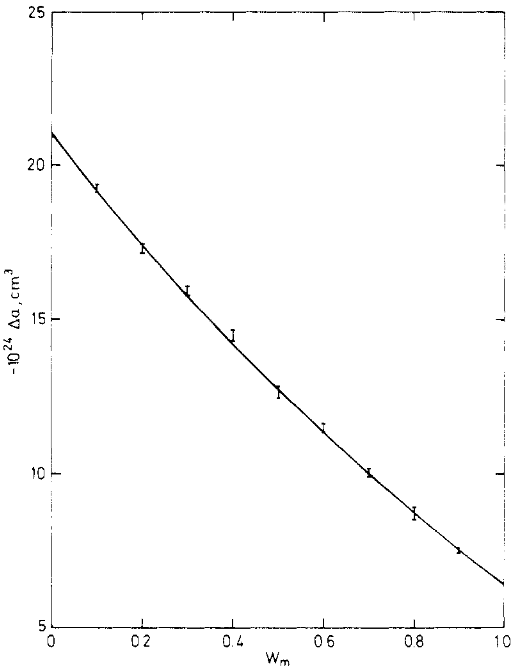

**Figure 8.** Optical-configuration parameter $\Delta a$ as a function of the fraction of meso diads $W_m$ calculated at 25 °C for chains consisting of $x = 100$ repeat units with energies of Table V and optical parameters described in the text.

**Table VI**
**Variation of $\Delta a$ with Temperature, Conformational Energies, and Optical Parameters Used in Calculations[a]**

| | $10^2[\mathrm{d}\Delta a/\mathrm{d(parameter)}]$ | | |
|---|---|---|---|
| parameter[b] | $W_m = 0$ | $W_m = 0.5$[c] | $W_m = 1.0$ |
| $T$ | 0.02 | -2.1 | -1.5 |
| $E_\sigma$ | 523.2 | 446.3 | 145.6 |
| $E_\omega$ | -14.1 | -10.1 | 8.8 |
| $E_{\omega'}$ | 339.3 | -382.8 | -116.6 |
| $E_{\omega''}$ | -1414.2 | -45.6 | 103.7 |
| $E_{\omega'''}$ | 518.2 | -59.0 | -124.0 |
| $E_\delta$ | 217.8 | 434.5 | 35.0 |
| $\Delta\alpha_{\mathrm{PhSi}}$ | -283.7 | -166.2 | -62.6 |
| $\Delta\alpha^+{}_{\mathrm{PhSi}}$ | 344.9 | 211.5 | 138.7 |
| $\Delta\alpha_{\mathrm{SiO}}$ | 501.3 | 302.9 | 232.7 |
| $\Delta\alpha_{\mathrm{SiCH_3}}$ | -217.3 | -136.4 | -170.0 |

[a] Dimensions: $\Delta a$ and optical parameters in $10^{-24}$ cm$^3$; energies in kcal/mol; $T$ in K. [b] The "main set" used was $T = 298$ K, energies of Table V, $x = 100$, $\Delta\alpha_{\mathrm{PhSi}} = 5.1$, $\Delta\alpha^+{}_{\mathrm{PhSi}} = -3.0$, $\Delta\alpha_{\mathrm{SiO}} = 1.3$, and $\Delta\alpha_{\mathrm{SiCH_3}} = 1.25$, in $10^{-24}$ cm$^3$ units. [c] Averages over 20 Monte Carlo chains.

exhibited by poly(methyl acrylate),[4] poly(vinyl acetate),[5] and poly(ethyl acetate)[6] and it is a consequence of the large and very anisotropic side groups of the chains, which produce negative components $\alpha_{xx}$ and $\alpha_{yy}$ in the $\hat{\alpha}_{i+1}$ tensor; those components give rise to negative contributions to the products $r^T\hat{\alpha}r$ that eventually overcome the positive contributions due to $\alpha_{xz}$ and $\alpha_{zz}$. As Table VI shows, a consequence of this situation is that an increase in the anisotropy of the side groups (i.e., an increase in $\Delta\alpha_{\mathrm{PhSi}}$ or $\Delta\alpha_{\mathrm{SiCH_3}}$ or an increase in the absolute value of $\Delta\alpha^+{}_{\mathrm{PhSi}}$) would decrease the value of $\Delta a$ (i.e., increase the absolute value of $\Delta a$), whereas an increase in $\Delta\alpha_{\mathrm{SiO}}$ raises the value of $\Delta a$.

**Table VII**
**Comparison of Experimental and Theoretical[a] Results at 25 °C**

| | $-10^{24}\Delta a$, cm$^3$ | $10^{26} \times (\mathrm{d}\Delta a/\mathrm{d}T)$, cm$^3$ K$^{-1}$ | $10^3 \times [\mathrm{d}(\ln \langle r^2\rangle_0)/\mathrm{d}T]$, K$^{-1}$ |
|---|---|---|---|
| | Experimental Results | | |
| unswollen | 12.1 | -2.4 | 0.6 |
| swollen | 8.5 | -1.7 | |
| | Theoretical Results | | |
| $E_\delta = -0.8$ | 11.6 | -2.7 | 2.2 |
| $E_\delta = -1.0$ | 12.6 | -2.1 | 1.6 |
| $E_\delta = -1.2$ | 13.3 | -1.4 | 1.0 |

[a] Averages over 20 Monte Carlo chains with $W_m = 0.5$ and the "main set" for all parameters (see Table V) except $E_\delta$ for which the stated energy (in kcal/mol) was used. [b] Swelling agent decalin; $v_2 = 0.204$ (see Table IV).

Table VII summarizes a comparison of our experimental and theoretical values of $\Delta a$ and the temperature coefficient of both $\Delta a$ and $\langle r^2\rangle_0$. The agreement between theory and experiment (for the unswollen sample) is excellent; in fact, to our knowledge, it is the best agreement found to date for $\Delta a$. Both $\Delta a$ and its temperature coefficient are almost exactly reproduced by taking $E_\delta = -0.9$ kcal/mol. However, the best fit for the temperature coefficient of the unperturbed dimensions requires[28] $E_\delta = -1.3$ kcal/mol. Therefore, the choice $E_\delta = 1.1 \pm 0.2$ kcal/mol gives good agreement for the three magnitudes summarized in Table VII.

As in the case of many other polymeric systems[2,4,5,12,20,21,29-31] the birefringence of the swollen samples is noticeably different from that exhibited by the unswollen network. Usually, the swollen sample presents smaller birefrigence than the unswollen one, and the agreement with theory is better if the results for the swollen sample are used for the comparison. However, this behavior has some exceptions. For instance, the stress-optical coefficient $C$ of poly(diethylene glycol terephthalate)[30] is increased by roughly 30% when the network is swollen with tricresyl phosphate, and, under these conditions the value of $\Delta a$ departs from the theoretical value even more than the value of the unswollen sample does. A similar situation was found with poly(dimethylsilamethylene) swollen with cyclic PDMS pentamer.[29] In the case of PMPS, the swelling of the network with decalin increases the value of $\Delta a$ (decreases its absolute value) by roughly 30% and it departs from the theoretical value. However, the theoretical value can be brought into agreement with the experimental result obtained in the swollen sample by an adequate adjustment of the parameters used in the calculations. As Table VI shows, if we keep the same geometry and energies used through all the calculations, the agreement can be achieved by decreasing the anisotropy of the side groups; for instance, a decrease of 1 Å in all these parameters (i.e., taking $\Delta\alpha_{\mathrm{SiPh}} = 4.1$, $\Delta\alpha^+{}_{\mathrm{SiPh}} = -2.0$, and $\Delta\alpha_{\mathrm{SiCH_3}} = 0.25$, all in units of $10^{-24}$ cm$^3$) is enough to obtain the agreement.

The discrepancy between theoretical and experimental results of $\Delta a$ found for many polymers when the same scheme of calculation and the same set of parameters give excellent results for other conformational properties, including Kerr constants,[32] whose calculation is formally identical with that of $\Delta a$, is usually attributed to the intermolecular correlations in the amorphous solid employed in the birefringence measurements. If this interpretation is valid, the present results for PMPS seem to suggest the following conclusions: (a) These correlations should be much smaller in asymmetric chains than in symmetric ones, since the agreement of theory and experiment is much better in the former case.[4,5,33] In fact, in the case of PMPS, the intermolecular correlations should be negligible. (b) The incorporation of a diluent into the network modifies the correlations between chains. However, the modification produced depends strongly on the kind of network and swelling agent used. In fact, a criterion from which one can estimate the most convenient diluent to be

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used has not been established yet, and usually, the most symmetric ones have been employed. In the case of PMPS, the modification seems to be in the sense of decreasing the anisotropy of the side group. A tentative explanation of the behavior of the swollen PMPS can be obtained if one imagines a solvation of the phenyl group by the diluent; the resulting solvated ring would be closer to spherical symmetry and hence less anisotropic than the unsolvated group.

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# Rigid-Rod Polyquinolines with Extended Aryl Ether Pendent Groups: An Approach to Solubility Enhancement

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ABSTRACT: Rigid-rod polyquinolines containing the pendent aryl ether groups $p\text{-C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{OC}_6\text{H}_5$, $p\text{-C}_6\text{H}_4\text{O-}p\text{-C}_6\text{H}_4\text{C}_6\text{H}_5$, and $p\text{-C}_6\text{H}_4\text{O-}p\text{-C}_6\text{H}_4\text{OC}_6\text{H}_5$ in the 4,4′ positions of the quinoline rings were prepared by the acid-catalyzed polymerization of the corresponding 3,3′-diaroylbenzidines with 4,4′-diacetylbiphenyl. These polyquinolines were crystalline ($T_m$ = 417–505 °C) and were not soluble in the more common organic solvents. The solubility of these polymers containing the pendent arms was similar to the analogous rigid-rod polymer containing pendent phenyl groups.

## Introduction

Although rigid-rod polyaromatics generally display high strength and possess the thermal and mechanical properties necessary for high-temperature applications, they have very limited solubility, or are insoluble, in common organic solvents. Thus they can be difficult to fabricate, and the study of their solution properties is often limited to solutions in strong acids. With a number of polyaromatics, solubility has been improved by the attachment of phenyl groups to the polymer main chain, as is the case with polyquinoxalines,[1] polyphenylenes,[2,3] and polyimides.[4] The solubility of a number of polyheterocycle/polyphenylene copolymers is enhanced by the attachment of phenoxyphenyl and phenylthiophenyl pendent groups.[5] However, improved solubility of the rigid-rod polybenzobis(oxazoles)[6] or polybenzobis(thiazoles)[7] was not realized through phenyl substitution on the phenylene units connecting the benzobis(oxazole) or benzobis(thiazole) units.

The rigid-rod polyquinoline poly[2,2′-(*p,p*′-biphenylene)-6,6-bi(4-phenylquinoline)] (1) has excellent thermal and mechanical properties, but it is soluble only in solvents such as trifluoromethanesulfonic acid and its polymerization medium, a mixture of *m*-cresol and di-*m*-cresyl phosphate.[8] Fibers spun from anisotropic solutions of 1 show an X-ray structure in which the parallel chains along the direction of the fiber axis stack in nearly coplanar

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