Stress-Optical Coefficient of *trans*-1, 4-Polybutadiene and *trans*-1, 4-Polyisoprene Networks

Measurements and Theoretical Interpretation

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ABSTRACT: Stress, strain, and birefringence measurements have been carried out on swollen and unswollen networks of *trans*-1,4-polybutadiene (*trans*-PBE) and *trans*-1,4-polyisoprene (*trans*-PIP), gutta percha. The average values of the optical anisotropy $\Delta\Gamma$ of Kuhn's random link for specimens swollen with solvents of optically and geometrically nearly isotropic molecules (simply, isotropic solvents) are 6.1 Å^3 for *trans*-PBE and 5.8 Å^3 for *trans*-PIP, while for unswollen specimens they are 8.6 Å^3 and 9.2 Å^3, respectively. For comparison, some measurements on swollen networks of *cis*-1,4-polyisoprene are included. The decrease in $\Delta\Gamma$ upon swelling with isotropic solvents, observed previously also for polyethylene and cis dienic polymers, is ascribed to the short-range orientational (parallel) order among polymer segments and solvent molecules, caused by the excluded volume and space-filling requirement. The unperturbed dimension $\langle r^2 \rangle$, $\Delta\Gamma$, and their temperature coefficients have been calculated for both *trans*-PBE and PIP, on the basis of conformational models explored by Mark and of theories developed previously by us. Alternative models for *trans*- and *cis*-PIP are presented from certain structure-geometric considerations. Theoretical values of $\Delta\Gamma$ are in close agreement with observed values obtained with isotropic solvents, provided statistical weight parameters adjusted to $\langle r^2 \rangle$ are combined with the anisotropic bond polarizabilities given by Clément and Bothorel, just as in the case of cis dienic polymers previously discussed.

KEY WORDS   *trans*-1,4-Polybutadiene and Polyisoprene / Simple Elongation / Stress-Optical Coefficient / Unperturbed Dimension / Rotational-Isomeric-State Model /

Stress-optical coefficients of polymeric networks, or equivalently the optical anisotropy $\Delta\Gamma$ of Kuhn's random link, can be calculated as a function of basic quantities characteristic of chain structures, *i.e.*, bond lengths, bond angles, potentials hindering rotations about skeletal bonds, and bond polarizabilities.[1-8] In earlier publications we have studied with some success a few polymers of relatively simple structures, *i. e.*, polyethylene,[1,4] poly-(dimethylsiloxane),[2] *cis*-1,4-polybutadiene (*cis*-PBE) and *cis*-1,4- polyisoprene (*cis*-PIP).[5] In this paper we treat *trans*-1,4-polybutadiene (*trans*-PBE) and *trans*-1,4-polyisoprene (*trans*-PIP).

No experimental data on stress-optical coefficients are available for *trans*-PBE. Saunders[9] reported photoelastic measurements on unswollen, peroxide-crosslinked samples of *trans*-PIP (in the form of gutta percha). Recent investigations[4,5,10] strongly suggest that intrinsic values

of $\Delta\Gamma$, *i.e.*, characteristic of isolated chains, are obtained with measurements on specimens swollen with solvents of geometrically and optically nearly isotropic molecules, rather than on unswollen specimens. We therefore decided to carry out photoelastic measurements on both *trans*-PBE and *trans*-PIP networks, laying emphasis on swollen specimens. Some measurements on swollen specimens of *cis*-PIP are included inasmuch as the paucity of relevant data left the analysis of this polymer inconclusive.[5] While this work was in progress we learned of work by Gent[11] on photoelastic measurements on swollen and unswollen specimens of *cis*- and *trans*-PIP. Close agreement was observed between his and our results for unswollen specimens and those swollen with the same solvents.

Random-coil conformations of *trans*-PBE and PIP were recently investigated by Mark,[12] in connection with the unperturbed mean-square

end-to-end distance $\langle r^2 \rangle$ and its temperature coefficient. His theoretical analysis provides a basis for interpretation of $\Delta\Gamma$. Trans and cis polymers differ only in the isomeric structures of double bonds and in rotational features of single bonds, the latter being a direct consequence of the former; bond lengths, bond angles, and bond polarizabilities are common for both polymers. A comparison of values of $\Delta\Gamma$ for trans polymers with those for cis polymers previously discussed,[5] should be of great interest, as was the case with $\langle r^2 \rangle$.[12,13]

MEASUREMENTS

Experimental

A raw rubber of *trans*-PBE, called *trans*-4 (a trade name of the Phillips Petroleum Co.) was kindly supplied by the Bridgestone Tire Co. The microstructure of this sample by infrared analysis is 91.9% 1,4-*trans*, 5.6% 1,4-*cis*, and 2.5% vinyl. The microstructure of *trans*-PIP, or gutta percha, is substantially 100% 1,4-*trans*. These samples were purified with activated charcoal powder in toluene solution and crosslinked with dicumyl peroxide. A sample of *cis*-PIP, Natsyn 2200 (a trade name of Goodyear Chemical; 97% 1,4-*cis* and others unknown) was vulcanized with sulfur. The recipes and conditions for crosslinking are given in Table I.

Table I. Recipes (parts in weight) and crosslinking conditions of samples

Sample	Trans-4	Gutta percha	Natsyn 2200
Polymer	100	100	100
ZnO	3	2	2
Stearic Acid	1	1	1
C.Z.[a]	0	0	1
H.T.[b]	0	0	1
D.T.B.C.[c]	0.5	0.5	0.5
M.B.M.B.P.[d]	0.5	0.5	0
Vulcanizing Agent	Dicup 2–3	Dicup 2–4	Sulfur 2
Time (min)	30	40	30
Temp. (°C)	155±5	155±5	145±5
Press. (kg/cm²)	30	30	30

[a] Cyclohexyl benzothiazyl sulfenamide, [b] Hexamethylene tetramine, [c] 2,6-Di-*tert*-butyl-*p*-cresol, [d] 2,2′-Methylene bis (4-methyl-6-*tert*-butylphenol).

Methods of preparation of specimens and of photoelastic measurements were previously[5] described in some detail and therefore have been largely omitted here. Some deviations from previous methods were made, which are described below. Measurements on swollen specimens were made while they were immersed in solvents, instead of being in a nitrogen atmosphere as in the previous case.[5] Prior to measurements specimens were subjected to equilibrium swelling with solvents, 2–4 hours being usually needed. Then specimens were stretched to the lowest elongation, and ten minutes later (the time usually needed for the tension recorder to become reasonably constant) the tension, length, and birefringence were recorded. Other elongations were examined similarly, with a cycle including the first increasing elongations and the subsequent decreasing elongations. After one cycle was completed, specimens were allowed to recover for about an hour without load, and then the swollen rest length l_{0s} was measured. After all measurements were finished, solvents in specimens were evaporated and the unswollen rest length l_0 was measured. The volume fraction v_r of polymer was determined as $(l_0/l_{0s})^3$. A possible variation of stress-optical coefficients which might arise from the change in v_r upon stretching, was checked by subsidiary measurements on some of specimens, while exposed in an air or nitrogen atmosphere, by using nonvolatile solvents. Results for the two types of measurements were in agreement within experimental error when maximum elongation ratios were limited to under 30%.

Refractive indices of unswollen specimens, measured with a high-temperature Abbe refractometer, were

$$n_D^T = 1.5229 - 0.366 \times 10^{-3}T \quad \text{for } \textit{trans}\text{-PBE}$$

$$n_D^T = 1.5305 - 0.385 \times 10^{-3}T \quad \text{for } \textit{trans}\text{-PIP}$$

with T in °C. Refractive indices of the swollen specimens were directly measured by using pieces which were cut from test specimens immediately after photoelastic measurements were completed.

Results

Stress-strain and birefringence-strain relations for the swollen specimens of *trans*-PBE are shown in Figures 1a and 1b, and for *trans*-PIP in Figures

2a and 2b, the data being plotted in accordance with the Mooney-Rivlin[14,15] relations with the suitable modification for swelling

$$v_r^{1/3} f(\lambda - \lambda^{-2})^{-1} = 2(C_1 + C_2\lambda^{-1}) \quad (1)$$

$$v_r^{-1/3} \Delta n(\lambda^2 - \lambda^{-1})^{-1} = B_1 + B_2\lambda^{-1} \quad (2)$$

where f is the stress referred to the unswollen, unstretched cross section; λ is the elongation ratio $\lambda = l/l_0$, l and l_0 being the lengths in the
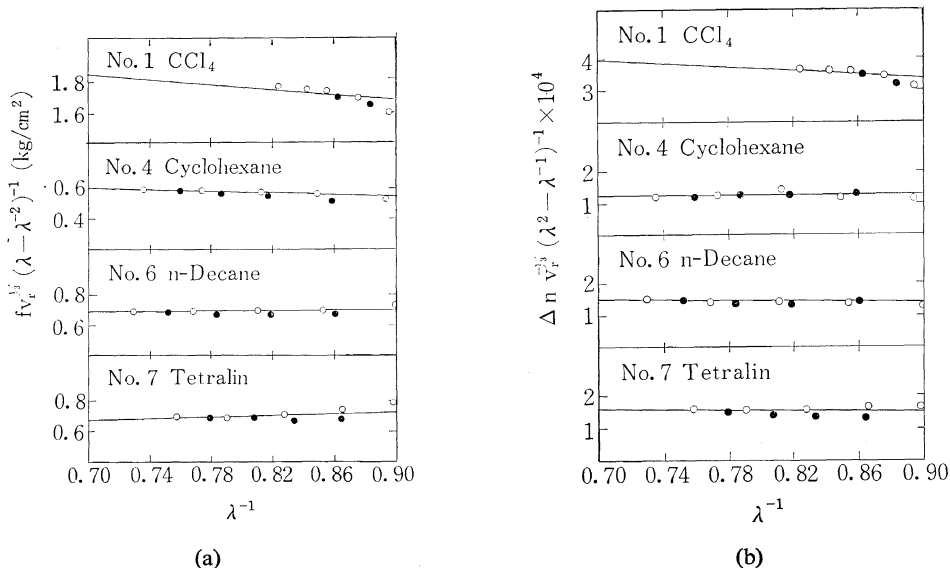

(a)   (b)

Figure 1. Moony-Rivlin plots for (a) stress-strain and (b) birefringence-strain relations for *trans*-PBE specimens swollen with various solvents indicated. Data points are on increasing (○) and decreasing (●) elongations. Code numbers are those in Table II.
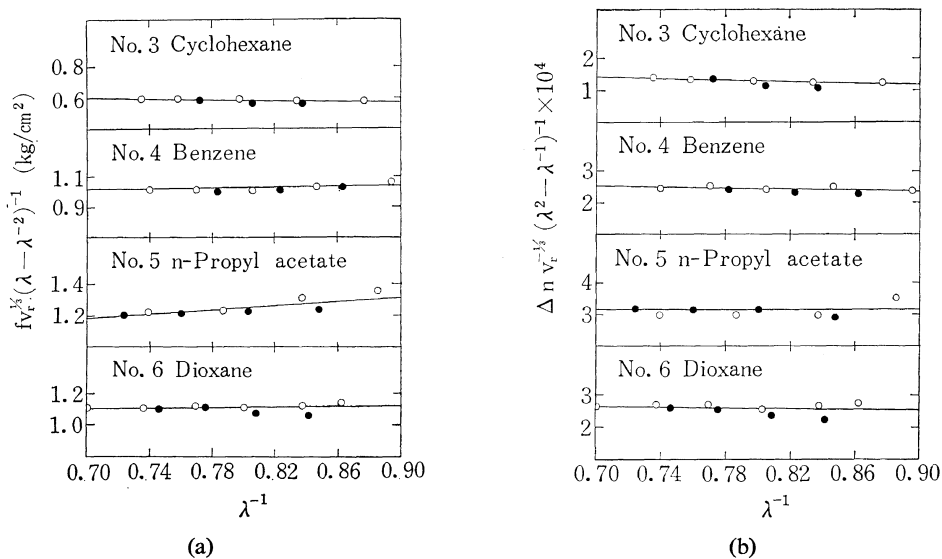

(a)   (b)

Figure 2. Moony-Rivlin plots for (a) stress-strain and (b) birefringence-strain relations for *trans*-PIP specimens swollen with various solvents indicated. Data points are on increasing (○) and decreasing (●) elongations. Code numbers are those in Table III.

presence and in the absence of applied load, respectively; Δn is the birefringence; and C_1, C_2, B_1, and B_2 are constants independent of λ. As seen in Figures 1 and 2, both stress-strain and birefringence-strain relations are reversible for increasing (○) and decreasing (●) elongations and non-Gaussian C_2 and B_2 terms are zero within experimental error, as was just the case with swollen specimens of *cis*-PBE previously investigated.[5] Quite the same behavior was observed for swollen specimens of *cis*-PIP although results are not reproduced here. The stress-optical coefficient C is given by

$$C = \frac{\Delta n}{\lambda v_r^{2/3} f} = \frac{B_1 + B_2 \lambda^{-1}}{2(C_1 + C_2 \lambda^{-1})} \tag{3}$$

According to Kuhn and Grün[16] and others,[17] C for the Gaussian network is given by

$$C = \frac{2\pi}{45kT} \cdot \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \Delta\Gamma \tag{4}$$

where $\bar{n}$ is the mean refractive index of a sample, k is the Boltzmann constant, T is the absolute temperature, and $\Delta\Gamma$ is the optical anisotropy of Kuhn's random link. We can calculate $\Delta\Gamma$ from experimental data through Eqs. 3 and 4. Average values of $\Delta\Gamma$ for *trans*-PBE and *trans*-PIP specimens unswollen and swollen with various solvents are summarized in Tables II and III, together with other pertinent data. Results for *cis*-PIP at 30°C are as follows: solvent, v_r, $\Delta\Gamma$ (Å³); CCl₄, 0.16, 4.05; benzene, 0.21, 4.14; *n*-decane, 0.32, 4.92; none, 1, 4.85. It is seen that our results for *trans*- and *cis*-PIP are in satisfactory agreement with those by Gent,[11] for the cases of specimens unswollen and swollen with the same solvents.

For later convenience we summarize experimental values of $\Delta\Gamma$ (and also of $\langle r^2 \rangle / n\bar{b}^2$) in Table IV. Values under heading "a" concern unswollen specimens, those under "b" specimens swollen with solvents of geometrically and optically nearly isotropic molecules (abbreviated hereafter "isotropic solvents"), and those under "c" are $\Delta\Gamma$ values obtained from flow-birefringence measurements by Poddubnyi, Erenburg, and Eryomina.[18] The value 6.1 Å³ for *trans*-PBE and the value 5.8 Å³ for *trans*-PIP are the averages of those for CCl₄, cyclohexane, and benzene, used

Table II. Average values of $\Delta\Gamma$ for swollen and unswollen specimens of *trans*-PBE

No.	Dicup[a]	Solvent	v_r	Temp. (°C)	$\bar{n}$	$\Delta\Gamma$(Å³)
1	2	CCl₄	0.12	60	1.444	5.83
2	3	CCl₄	0.18	60	1.449	5.79
3	3	benzene	0.19	60	1.482	6.29
4	2	cyclohexane	0.11	60	1.414	6.45
5	3	decalin	0.19	80	1.460	6.34
6	2	*n*-decane	0.16	80	1.399	6.62
7	2	tetralin	0.10	60	1.520	6.13
8	2	tetralin	0.10	70	1.515	6.41
9	2	tetralin	0.10	80	1.510	6.77
10	2	———	1.00	95	1.488	8.56

[a] Parts in weight of Dicup to 100 parts of polymer; see Table I.

Table III. Average values of $\Delta\Gamma$ for swollen and unswollen specimens of *trans*-PIP

No.	Dicup[a]	Solvent	v_r	Temp. (°C)	$\bar{n}$	$\Delta\Gamma$(Å³)
1	2	CCl₄	0.09	40	1.454	5.29
2	3	CCl₄	0.15	40	1.458	5.42
3	2	cyclohexane	0.11	40	1.425	6.09
4	2	benzene	0.13	40	1.490	6.25
5	2	*n*-propyl acetate	0.28	60	1.405	7.48
6	2	dioxane	0.29	48	1.438	6.51
7[b]	2	*n*-decane	0.11	40	1.418	6.87
8	2	*n*-decane	0.20	40	1.425	7.32
9	4	*n*-decane	0.29	40	1.431	7.16
10	2	tetralin	0.12	40	1.529	6.73
11	2	tetralin	0.12	50	1.524	6.95
12	2	tetralin	0.12	60	1.520	7.34
13	2	——	1.00	65	1.505	9.15

[a] Parts in weight of Dicup to 100 parts of polymer; see Table I.
[b] Crosslinking time is 20 minutes.

as solvents, while the value 4.1 Å³ for *cis*-PIP is the average of those for CCl₄ and benzene.

In Table IV included are experimental values of $\langle r^2 \rangle / n\bar{b}^2$, where n is the number of skeletal bonds and $\bar{b}^2$ is the mean-square skeletal bond length, i.e., $\bar{b}^2 = (1/4)(b_i^2 + 2b_{i+1}^2 + b_{C=C}^2)$, (see Figure 3 and Table V). Mark[19] reported $\langle r^2 \rangle / n\bar{b}^2 = 5.8$ for *trans*-PBE in decalin at 55°C. Mark[12] estimated $\langle r^2 \rangle / n\bar{b}^2 = 7.35$ for gutta percha in *n*-propyl acetate at 60°C (a θ-solvent) from work by Wagner and Flory[20] on the intrinsic viscosity

Table IV. Comparison of experimental values of $\Delta\Gamma$ and $\langle r^2 \rangle/n\bar{b}^2$ for *trans-* and *cis*-PBE and PIP

| | $\Delta\Gamma(\text{Å}^3)$ | | | $\langle r^2 \rangle/n\bar{b}^2$ |
	a	b	c	
trans-PBE	8.6[b]	6.1[d]	7.1	5.8[g]
trans-PIP	9.2[d], 9.1[e], 9.4[f]	5.8[d], 5.9[f]	4.9	7.35[h], 6.55[i]
cis-PBE	7.5[d]	5.8[d]	6.3	4.9[j]
cis-PIP	4.9[d], 4.7[e], 4.8[f]	4.1[d], 4.0[f]	4.8	4.7[k]

[a] On unswollen specimens, [b] On specimens swollen with isotropic solvents, [c] Flow-birefringence data of Poddubnyi *et al.*,[18] [d] Our data, this work and ref. 5., [e] Saunders,[9] [f] Gent,[11] [g] Thomas and Mark,[19] [h] Wagner and Flory[20] and Mark,[13] [i] Poddubnyi *et al.*,[18] [j] Mark,[12] [k] Wagner and Flory,[20] and Mark[12]

$[\eta]$ versus molecular weight M relations. Very recently, Poddubnyi *et al.*[18] reported $[\eta]_\theta = 1.91 \times 10^{-3}M^{0.5}$ in dioxane at 47.7°C (a θ-solvent). From this relation we estimate $\langle r^2 \rangle/n\bar{b}^2 = 6.55$, according to Flory and Fox's method[21] by using $\Phi = 2.5 \times 10^{21}$. The difference may be due either to the specific solvent effect on the unperturbed dimension or to experimental error. The newer value[18] appears more accurate, judging from a larger number of experimental points and the smoothness of them in the log $[\eta]_\theta$-log M plot.

Discussion

As seen in Tables II–IV, $\Delta\Gamma$ for trans polymers decreases considerably when networks are swollen with isotropic solvents, just as in the case of the *cis*-PBE previously studied.[5] Quite the same behavior was reported by Gent for polyethylene[10] and *cis*- and *trans*-PIP.[11] As previously,[22,4,5] we interpret this effect as follows. There may exist a short-range orientational order among polymer chain segments in a condensed phase of long-chain molecules, because of the excluded-volume effect and space-filling requirement. The noted decrease in $\Delta\Gamma$ is due to the fact that the order existing in bulk state decreases with increasing swelling, and vanishes beyond a certain degree of swelling. The value of $\Delta\Gamma$ at the latter condition is considered to be its intrinsic value characteristic of an isolated chain. The degree of decrease in $\Delta\Gamma$ is more pronounced in the order of *cis*-PIP (16%), *cis*-PBE (23%), *trans*-PBE (30%), and *trans*-PIP (36%). This degree is presumed to qualitatively reflect the degree of the orientational order existing in bulk state. On the other hand, from an intuitive consideration, the orientational order should increase with increasing smoothness in a chain contour (*i.e.*, the absence

of pendant groups) and with increasing chain stiffness (or $\langle r^2 \rangle/n\bar{b}^2$). Qualitatively, the observed degrees of decrease in $\Delta\Gamma$ are compatible with this method of criterion, as can readily be confirmed from Table IV. For comparison, the decrease in $\Delta\Gamma$ for polyethylene is *ca.* 55%[10] and $\langle r^2 \rangle/n\bar{b}^2 = 6.7$.[23] When specimens are swollen with anisotropic solvents, the order among polymer segments is replaced by that between polymer segments and solvent molecules, and the intrinsic $\Delta\Gamma$ is masked by the contribution from solvent molecules that are indirectly oriented through the ordering interaction with network chains. This consideration accounts for the result in Tables II and III that $\Delta\Gamma$ is larger in anisotropic solvents than in isotropic solvents. It is interesting that the effect of anisotropic solvents in increasing $\Delta\Gamma$ over that for isotropic solvents is greater for *trans*-PIP than for *trans*-PBE; for example, with *n*-decane, the respective values of $\Delta\Gamma(\text{Å}^3)$ are 7.1 versus 5.8 for *trans*-PIP, but 6.6 versus 6.1 for *trans*-PBE. This result is understandable because, with the same solvent, the short-range order between polymer segments and solvent molecules should be stronger for a stiffer chain.

The idea described above was recently placed on the confirmative basis by Gent.[11] He extensively investigated the influence of solvents on $\Delta\Gamma$ for *cis*- and *trans*-PIP, using a variety of solvents which differ markedly in geometrical asymmetry, in optical anisotropy, and in refractive index. He found that $\Delta\Gamma$ increases with increasing geometrical asymmetry in accordance with the idea described above, and eventually rejected convincingly other possible mechanisms on the solvent dependence of $\Delta\Gamma$, such as the "form

effect", discussed by Tsvetkov.[24] The same idea was previously proposed by Frisman and coworkers[25] for interpretation of the solvent dependence of $\Delta\Gamma$ observed in flow-birefringence measurements on dilute polymer solutions.

From No. 1, 2, 7 to 9 of Table III, we observe that $\Delta\Gamma$ is independent of v_r within experimental error. We can assume therefore that the short-range orientational order does not vary by dilution beyond $v_r = 0.3$ and vanishes in isotropic solvents. The range of $v_r < 0.3$ is that to which our measurements are limited. The solvents used cover a certain range of the solvent power, but no correlation is observed between the solvent power (judged from v_r^{-1}) and $\Delta\Gamma$. (We note that *n*-propyl acetate at 60°C and dioxane at 48°C are θ-solvents for *trans*-PIP.) This is true with the results of Gent.[11] We conclude therefore that the short-range orientational order is dominant over the solvent power in determining $\Delta\Gamma$.

Attempts to measure the temperature coefficient of $\Delta\Gamma$ for unswollen specimens were met with difficulty because above melting points both polymers, in particular *trans*-PBE, suffered from thermal degradation accompanied with decreasing transparency even under the nitrogen atmosphere. For *trans*-PIP we obtained on the average $d\ln\Delta\Gamma/dT = -0.38 \times 10^{-3}$ deg^{-1} at $\lambda = 1$ in the range 65—85°C, which is compared with -0.87×10^{-3} deg^{-1} estimated from data of Saunders.[9] Values of $d\ln\Delta\Gamma/dT$ for specimens swollen with tetralin were estimated from No. 7 to 9 of Table II and No. 10 to 12 of Table III, yielding 4.93×10^{-3} deg^{-1} for *trans*-PBE and 4.34×10^{-3} deg^{-1} for *trans*-PIP. Positive temperature coefficients were found also for specimens swollen with carbon tetrachloride. For the present, however, we

have reservations about accepting either of these values as intrinsic values because of the possible short-range orientational order, as well as experimental error.

THEORETICAL INTERPRETATION

Structural and Polarizability Parameters and Statistical Weight Matrices

A portion of the *trans*-PIP chain is depicted in Figure 3, with the definition of structural parameters. Replacement of the methyl group by a hydrogen atom yields the *trans*-PBE chain. Values of these parameters that we used are given in Table V. For the anisotropic bond polarizabilities $(\alpha_1 - \alpha_2)_{C\text{-}C}$, $(\alpha_1 - \alpha_2)_{C\text{-}H}$, and $(\alpha_1 - \alpha_2)_{C=C}$, we examined the three sets given in Table VI, as in the case of cis dienic polymers.[5] For the methyl

Table V. Bond lengths, bond angles, and rotational states

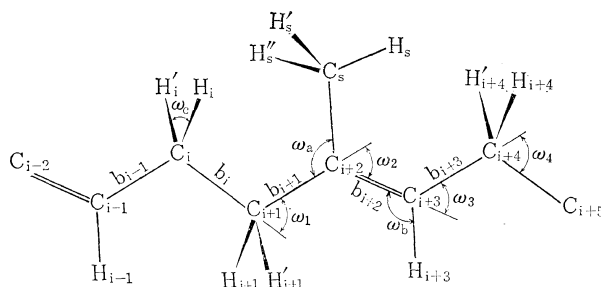| Type	Symbol	Bond length (Å)	Bond angle (deg)	Rotational state (deg)
$b_{C\text{-}C}$	b_i	1.53		
	b_{i+1}, b_{i+3}	1.51		
$b_{C=C}$	b_{i+2}	1.34		
$\angle CH_2\text{-}CH_2\text{-}CR^a$	$\pi - \omega_1$		112	
$\angle CH\text{-}CH_2\text{-}CH_2$	$\pi - \omega_4$		112	
$\angle CH_2\text{-}CR=CH$	$\pi - \omega_2$		125	
$\angle CR=CH\text{-}CH_2$	$\pi - \omega_3$		125	
$\angle CH_2\text{-}C\text{-}R$	ω_a		117.5	
$\angle CR=C\text{-}H$	ω_b		117.5	
$\angle H\text{-}C\text{-}H$	ω_c		109.5	
$CH_2\text{-}CH_2$	θ_i			0, ±120
$CH_2\text{-}CR$	θ_{i+1}			±60, 180
$CH\text{-}CH_2$	θ_{i+3}			±60, 180
$CR\text{-}CH$	θ_{i+2}			0

^{a} R $\equiv$ CH$_3$.

Figure 3. Portion of the *trans*-PIP chain with the definition of structural parameters.

C–C bond of *trans*-PIP we used the relation $(\alpha_1 - \alpha_2)_{\text{C-CH}_3} = (\alpha_1 - \alpha_2)_{\text{C-C}} - (\alpha_1 - \alpha_2)_{\text{C-H}}$ as previously.[5]

Following Mark,[12] we assume that θ_i is in the trans (T, $\theta^{(T)} = 0°$), the gauche (G, $\theta^{(G)} = 120°$), or the other gauche (G', $\theta^{(G')} = -120°$) conformation, that θ_{i+1} and θ_{i+3} are in the skew (S, $\theta^{(S)} = 60°$), the other skew (S', $\theta^{(S')} = -60°$), or the cis (C, $\theta^{(C)} = 180°$) conformation, and that θ_{i+2} is fixed at the trans (T, $\theta^{(T)} = 0°$) conformation. Here the internal rotational angle θ is measured from the trans position toward the direction of the right-handed twist of a polymer chain. Since the number of accessible states for each rotatable bond is three, our statistical weight matrices are of order three. We follow Mark[12] in the notation for statistical weights. The statistical weight matrices, P_1 between θ_i and θ_{i+1}, P_2 between θ_{i+1} and θ_{i+2}, P_3 between θ_{i+2} and θ_{i+3}, and P_4 between θ_{i+3} and θ_{i+4}, can be shown as follows

$$\lambda P_1 = \begin{array}{c|ccc} {}_{\theta_i}\!\diagdown^{\theta_{i+1}} & S & S' & C \\ \hline T & 1 & 1 & \alpha^{1/2} \\ G & \sigma^{1/2} & \sigma^{1/2} & (\alpha\sigma)^{1/2}\beta \\ G' & \sigma^{1/2} & \sigma^{1/2} & (\alpha\sigma)^{1/2}\beta \end{array} \quad (5)$$

$$P_2 = \begin{array}{c|ccc} {}_{\theta_{i+1}}\!\diagdown^{\theta_{i+2}} & T & A & A' \\ \hline S & 1 & 0 & 0 \\ S' & 1 & 0 & 0 \\ C & \alpha^{1/2} & 0 & 0 \end{array} \quad (6)$$

$$P_3 = \begin{array}{c|ccc} {}_{\theta_{i+2}}\!\diagdown^{\theta_{i+3}} & S & S' & C \\ \hline T & 1 & 1 & \alpha^{1/2}\delta_B \\ A & 0 & 0 & 0 \\ A' & 0 & 0 & 0 \end{array} \quad (7)$$

$$P_4 = \begin{array}{c|ccc} {}_{\theta_{i+3}}\!\diagdown^{\theta_{i+4}} & T & G & G' \\ \hline S & 1 & \sigma^{1/2} & \sigma^{1/2} \\ S' & 1 & \sigma^{1/2} & \sigma^{1/2} \\ C & \alpha^{1/2}\delta_B & (\alpha\sigma)^{1/2}\beta\delta_B & (\alpha\sigma)^{1/2}\beta\delta_B \end{array} \quad (8)$$

Table VI. Anisotropic bond polarizabilities

Anisotropic bond polarizabilities (Å^3)			Reference
$(\alpha_1 - \alpha_2)_{\text{C-C}}$	$(\alpha_1 - \alpha_2)_{\text{C-H}}$	$(\alpha_1 - \alpha_2)_{\text{C=C}}$	
1.86	0.21	1.80	Denbigh[30]
0.72	0	2.05	Le Fevre[31]
1.42	0.22	3.04	Clément and Bothorel[32]

where λ is the largest eigenvalue of $\lambda P_1 P_2 P_3 P_4$ and is introduced to normalize $P_1 P_2 P_3 P_4$ so that its largest eigenvalue becomes unity. In Eqs. 6 and 7 A and A' are arbitrary states which are introduced to make both P_2 and P_3 the square matrices of order three. δ_B equals unity for *trans*-PBE and zero for *trans*-PIP. σ is the statistical weight of the gauche state relative to the trans about bond i, α is that of the cis relative to the skew about bonds $i + 1$ and $i + 3$, and β is the statistical weight associated with the two-bond interaction involved in the GC or $G'C$ conformation of the bond pairs θ_i and θ_{i+1} as well as θ_{i+3} and θ_{i+4}. The elimination of the cis state of bond $i + 3$ for *trans*-PIP is due to the severe, steric interaction involved in this conformation.[12] The random-coil conformations of the *trans*-PBE and PIP chains in terms of the parameters mentioned above, due to Mark,[12] involves a somewhat oversimplified description of the interactions in some combinations of rotational states about bonds $i - 1$, i, and $i + 1$, as pointed out by Flory[26] (see also later), but is useful as the first approximation.

In the interest of reducing orders of matrices we employ the structural-symmetry method,[27] often used previously,[2,5] as follows

$$P_{1+} = \lambda^{-1}\begin{pmatrix} 2^{1/2} & \alpha^{1/2} \\ 2\sigma^{1/2} & (2\alpha\sigma)^{1/2}\beta \end{pmatrix} \quad P_{1-} = 0 \quad (9)$$

$$P_{2+} = \begin{pmatrix} 2^{1/2} & 0 \\ \alpha^{1/2} & 0 \end{pmatrix} \quad P_{2-} = 0 \quad (10)$$

$$P_{3+} = \begin{pmatrix} 2^{1/2} & \alpha^{1/2}\delta_B \\ 0 & 0 \end{pmatrix} \quad P_{3-} = 0 \quad (11)$$

$$P_{4+} = \begin{pmatrix} 2^{1/2} & 2\sigma^{1/2} \\ \alpha^{1/2}\delta_B & (2\alpha\sigma)^{1/2}\beta\delta_B \end{pmatrix} \quad P_{4-} = 0 \quad (12)$$

The temperature coefficients of $\langle r^2 \rangle$ and $\Delta\Gamma$ are calculated by assuming the Boltzmann relation

$$\sigma = \exp(-F_\sigma/RT) = \exp(S_\sigma/R)\exp(-E_\sigma/RT) \quad (13)$$

where F_σ, S_σ, and E_σ are the free energy, entropy, and energy differences, respectively, and R is the gas constant. Then following equations are obtained.

$$\frac{d\ln\langle r^2\rangle}{dT} = \frac{1}{RT^2}\left(E_\sigma\frac{\partial\ln\langle r^2\rangle}{\partial\ln\sigma}\right.$$
$$\left. + E_\alpha\frac{\partial\ln\langle r^2\rangle}{\partial\ln\alpha} + E_\beta\frac{\partial\ln\langle r^2\rangle}{\partial\ln\beta}\right) \quad (14)$$

$$\frac{d\ln\varDelta\Gamma}{dT} = \frac{1}{RT^2}\left(E_\sigma\frac{\partial\ln\varDelta\Gamma}{\partial\ln\sigma}\right.$$
$$\left. + E_\alpha\frac{\partial\ln\varDelta\Gamma}{\partial\ln\alpha} + E_\beta\frac{\partial\ln\varDelta\Gamma}{\partial\ln\beta}\right) \quad (15)$$

We briefly refer to experimental and theoretical evidence on values of the various parameters. From the analysis of the unperturbed dimension and its temperature coefficient, Mark[13] estimated $E_\sigma = -0.2$ kcal/mol for *cis*-PBE and $E_{\sigma'} = -0.6$ kcal/mol for *cis*-PIP. (In Mark's treatments[12,13] the σ value for *cis*- and *trans*-PBE was assumed to differ from that for *cis*- and *trans*-PIP, the latter being designated as σ'.) From the analysis of the unperturbed dimension and stress-optical coefficient we obtained $E_\sigma = 0.2$ kcal/mol and $E_{\sigma'} = -0.18$ kcal/mol for the respective polymers.[5] In the paper[12] treating trans polymers Mark revised E_σ as $E_\sigma = 0$, based on some energetical considerations. From the analysis of the unperturbed dimension and its temperature coefficient of *trans*-PBE and PIP, he estimated $E_\alpha = 0.03$ kcal/mol, $E_\beta = 1.1$ kcal/mol, and $E_{\sigma'} = 0.4$ kcal/mol. (In this treatment, Mark assumed that E_α and E_β should be common for *trans*-PBE and *trans*-PIP.) From infrared measurements Ciampelli[28] estimated $E_\sigma = 0.2$, 0, and 0.4 kcal/mol for 1,5-hexadiene, *cis*- and *trans*-PBE, respectively. Shimanouchi and Abe[29] investigated the rotational isomerism in model compounds for isoprene polymers by infrared measurements. Values of E_α were considerably divergent $(0\sim-0.8$ kcal/mol), depending on compounds and states (liquid or gas). For 2-methyl-1-pentene they found $E_\alpha \simeq -0.8$ kcal/mol and $E_\beta \simeq 0.3$ kcal/mol, which give $\alpha \simeq 3.9$ and $\beta \simeq 0.6$ at 20°C. In all theoretical treatments of polymers[12,13,28] and model compounds[28,29] it was assumed that $S_\sigma = S_\alpha = S_\beta = 0$. We follow this convention though evidence

is not sufficient except for S_σ.[5]

Numerical Results, Comparison with Experiment, and Discussion

All numerical computations were carried out using a program written previously.[5] The necessary theoretical expressions were given in the previous paper.[5] Recently more (probably the most) compact expressions were derived for $\langle r^2\rangle$ and $\varDelta\Gamma$ by one of the present authors.[6]

In order to examine the adequacy of the three sets of anisotropic bond polarizabilities given in Table VI, we first calculated $\varDelta\Gamma$ for the *trans*-PBE chain for the three sets by using statistical weights proposed by Mark[12]: $\sigma = 1$, $\alpha = 0.96$, and $\beta = 0.24$. Results were 7.00 Å^3 for Denbigh's set,[30] 4.03 Å^3 for Le Fevre's set,[31] and 6.15 Å^3 for Clement and Bothorel's set.[32] The latter value is in fair agreement, but the first two are not, with the (average) value 6.1 Å^3 observed with isotropic solvents. Quite the same situation was experienced in the case of *cis*-PBE.[5] For this reason and another given previously (ref. 5, p. 1141), we decided to carry out extensive calculations only for Clément and Bothorel's set.[32]

We first consider the *trans*-PBE chain. Mark[12] assumed $\sigma = 1$ on the basis of a qualitative consideration on steric interactions involved in the trans and gauche conformations of bond i. Following him we adopt $\sigma = 1$. The analysis of $\langle r^2\rangle$ of the *cis*-PBE chain indicates $E_\sigma \simeq 0$ or $\sigma \simeq 1$.[5,13] Values of $\langle r^2\rangle$ and $\varDelta\Gamma$ for the *trans*-PBE chain are plotted against $-\ln\alpha$ for $\sigma = 1$ and selected values of β in Figures 4a and 4b. As is obvious from Figure 4a, an infinite number of sets of α and β are compatible with the observed value $\langle r^2\rangle/n\bar{b}^2 = 5.8$. A unique determination could be made in principle by using the temperature coefficient of $\langle r^2\rangle/n\bar{b}^2$ obtained from stress-temperature measurements on unswollen networks, as done by Mark.[12] Unfortunately this method is subject to a considerable uncertainty, as we discussed in detail previously.[5] Values of α estimated from model compounds[29] are divergent though suggesting $\alpha > 1$. Under this circumstance we choose somewhat arbitrarily $\alpha = 1$; the harmonized value of β that reproduces the observed characteristic ratio is $\beta = 0.25$. This set of α and β is close to that determined by Mark[12]: $\alpha = 0.96$ and $\beta = 0.24$. Table VII in-
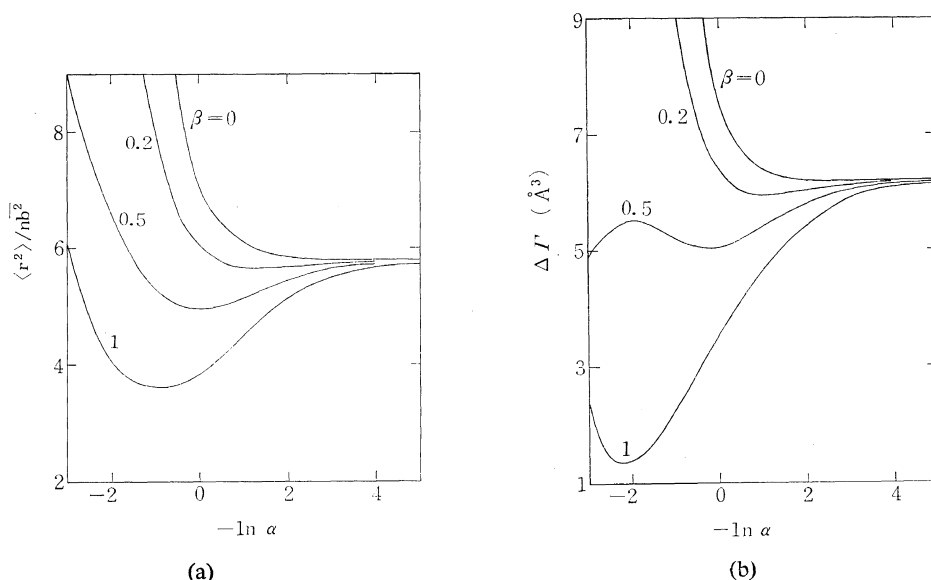
Figure 4. (a) $\langle r^2 \rangle / n\bar{b}^2$ and (b) $\Delta\Gamma$ vs. $-\ln\alpha$, for the *trans*-PBE chain. Clément and Bothorel's set[32] of anisotropic bond polarizabilities is used.

Table VII. Calculated (at 100°C) and observed values of $\langle r^2 \rangle / n\bar{b}^2$, $\Delta\Gamma$ and their temperature coefficients for the *trans*-PBE chain[a]

	Calculated			Observed
	Set 1	Set 2	Set 3	
α	1	1	1	
β	0.25	0.45	0.08	
E_β (kcal/mol)	1.03	0.59	1.87	
σ	1	0.763	1.31	
E_σ (kcal/mol)	0	0.20	−0.20	
$\langle r^2 \rangle / n\bar{b}^2$	5.804	5.850	5.847	5.8[b]
$d\ln\langle r^2 \rangle / dT$ $\times 10^3$ (deg^{-1})	−0.667	−1.012	−0.149	−0.65[b]
$\Delta\Gamma$(Å^3)	6.136	6.284	6.066	6.1[c]
$d\ln\Delta\Gamma / dT$ $\times 10^3$ (deg^{-1})	−0.753	−2.786	−0.101	4.93[d]

[a] Clément and Bothorel's set[32] of anisotropic bond polarizabilities is used. It is assumed that $S_\alpha = S_\beta = S_\sigma = 0.$, [b] Mark,[12] [c] Average value for specimens swollen with isotropic solvents, this work, [d] Value for specimens swollen with tetralin, this work.

cludes calculated values of $\langle r^2 \rangle / n\bar{b}^2$, $\Delta\Gamma$, and their temperature coefficients for three sets of parameters including that given above, together with experimental values. Sets 2 and 3 examine

the influence of small deviations of E_σ from zero. It is interesting that these sets of parameters which were adjusted to reproduce the observed value of $\langle r^2 \rangle / n\bar{b}^2$, yield very similar values of $\Delta\Gamma$, despite considerable differences in values of individual parameters. These calculated values are notably in fair agreement with the experimental value of $\Delta\Gamma$ obtained with isotropic solvents.

We next consider the *trans*-PIP chain. Values of $\langle r^2 \rangle / n\bar{b}^2$ and $\Delta\Gamma$ are plotted against $-\ln\sigma'$ for several combinations of α and β in Figures 5a and 5b. Here Clément and Bothorel's set[32] of anisotropic bond polarizabilities was used. It is seen that $\langle r^2 \rangle / n\bar{b}^2$ and $\Delta\Gamma$ behave very similarly as σ' is varied. According to Mark[12] α and β should be common for both *trans*-PBE and PIP. If therefore we use $\alpha = 1$ and $\beta = 0.25$, the value of σ' that yields $\langle r^2 \rangle / n\bar{b}^2 = 6.55$ by Poddubnyi *et al.*[18] is 0.67. These values of parameters combined with the three set of anisotropic bond polarizabilities give the following values of $\Delta\Gamma$ (all in Å^3): 6.21 for Clément and Bothorel's set,[32] 6.57 for Denbigh's,[30] and 4.04 for Le Fevre's.[31] The first of these is close to the value 5.8Å^3 obtained with isotropic solvents. On the other hand, the value of σ' that yields $\langle r^2 \rangle / n\bar{b}^2 = 7.35$ by Wagner and Flory[20] is $\sigma' = 0.536$ (together with $\alpha = 1$
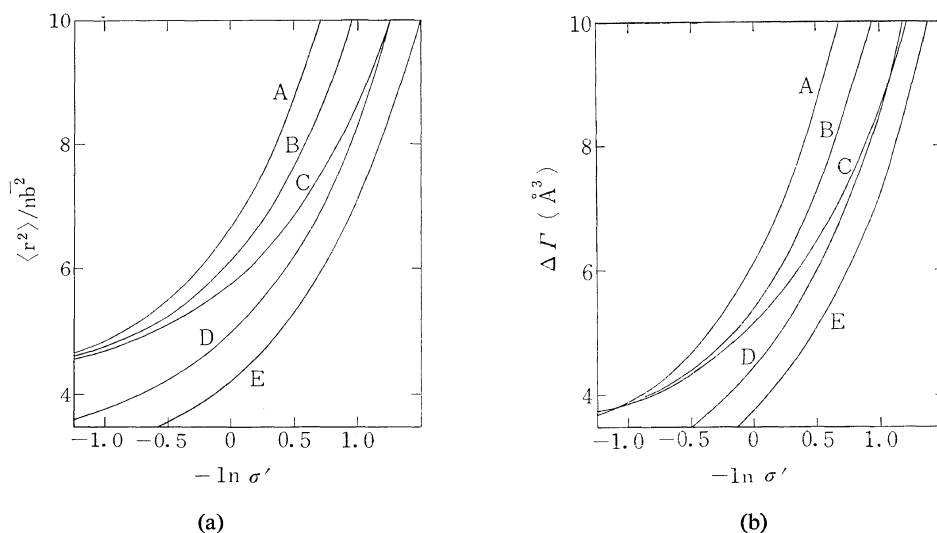
(a)

(b)

Figure 5. (a) $\langle r^2 \rangle / n\bar{b}^2$ and (b) $\Delta\Gamma$ vs. $-\ln \sigma'$, for the *trans*-PIP chain. A: $\alpha = 2$, $\beta = 0$. B: $\alpha = 1$, $\beta = 0$. C: $\alpha = 0$, $\beta = 0$. D: $\alpha = 1$, $\beta = 0.5$. E: $\alpha = 1$, $\beta = 1$. Clément and Bothorel's set[32] of anisotropic bond polarizabilities is used.

Table VIII. Calculated (at 60°C) and observed values of $\langle r^2 \rangle / n\bar{b}^2$, $\Delta\Gamma$, and their temperature Coefficients for the *trans*-PIP chain[a]

		Calculated			Observed
		Set 1	Set 2	Set 3	
	α	1	1	1.46	
E_α	(kcal/mol)	0	0	-0.25	
	β	0.25	0.25	0	
E_β	(kcal/mol)	0.92	0.92	∞	
	σ'	0.670	0.536	0.942	
$E_{\sigma'}$	(kcal/mol)	0.26	0.41	0.04	
$\langle r^2 \rangle / n\bar{b}^2$		6.544	7.353	6.537	7.35,[b] 6.55[c]
$d \ln \langle r^2 \rangle / dT$ $\times 10^3$ (deg^{-1})		-1.01	-1.45	-0.07	-0.27[d]
$\Delta\Gamma$(Å^3)		6.206	7.194	5.959	5.8[e]
$d \ln \Delta\Gamma / dT$ $\times 10^3$ (deg^{-1})		-1.18	-1.71	-0.09	4.34[f]

[a] Clément and Bothorel's set of anisotropic bond polarizabilities is used. It is assumed that $S_\alpha' = S_\beta' = S_{\sigma'} = 0$., [b] Estimated by Mark[12] from data of Wagner and Flory,[20] [c] Estimated from data of Poddubnyi *et al.*,[18] [d] Mark,[12] [e] Values for specimens swollen with isotropic solvents, ref. 11 and this work, [f] Value for specimens swollen with tetralin, this work.

and $\beta = 0.25$). These values of parameters combined with the above three sets of anisotropic

bond polarizabilities give $\Delta\Gamma = 7.19$, 7.95, and 4.61Å^3, respectively. The preference of $\langle r^2 \rangle / n b^2 = 6.55^{18}$ is apparent. Table VIII includes calculated results for the typical sets of statistical weight parameters together with experimental values.

We wish to supplement the previous analysis of the *cis*-PIP chain. According to Mark,[12] σ' should be common for *trans*- and *cis*-PIP. Use of $\sigma' = 0.67$ determined above, instead of the previous $\sigma' = 1.35$, in ref. 5, Table VII, Set 3, yields $\langle r^2 \rangle / n\bar{b}^2 = 4.953$, $d \ln \langle r^2 \rangle / dT = -0.092 \times 10^{-3}$ deg^{-1}, $\Delta\Gamma = 5.011$ Å^3, and $d \ln \Delta\Gamma / dT = -0.187 \times 10^{-3}$ deg^{-1}, compared with the previous results $\langle r^2 \rangle / n\bar{b}^2 = 4.71$ and $\Delta\Gamma = 4.53$ Å^3. This change in σ' makes both $\langle r^2 \rangle / n\bar{b}^2$ and $\Delta\Gamma$ somewhat more deviate from their experimental values $\langle r^2 \rangle / n\bar{b}^2 = 4.7$ and $\Delta\Gamma = 4.1$ Å^3 for isotropic solvents (Table IV).

Theoretical expressions of $\Delta\Gamma$ for the four dienic polymers can be cast into

$$\Delta\Gamma = \sum_\kappa F_\kappa (\alpha_1 - \alpha_2)_\kappa \qquad (16)$$

where the summation on κ extends over the four types of bonds, C–C, C=C, C–H, and C–CH$_3$. Values of the coefficients F_κ for representative sets of statistical weight parameters for the four polymers are given in Table IX. These values are

Table IX. Coefficients F_κ in eq. (16) for representative sets of statistical weight parameters for the four dienic polymers

	F_{C-C}	$F_{C=C}$	F_{C-H}	F_{C-CH_3}	Source of statistical weight parameters
trans-PBE	3.730	0.647	−5.126	0	Table VII, Set 1
trans-PIP	4.097	0.859	−5.006	−0.934	Table VIII, Set 1
cis-PBE	0.894	1.683	−3.664	0	Ref. 5, Table VI, Set 1
cis-PIP	0.917	1.536	−3.009	−0.653	Ref. 5, Table VII, Set 3

useful for the purpose of obtaining results for other anisotropic bond polarizabilities. It is seen that the partition of the contributions from C–C and C=C to $\Delta\Gamma$ is quite different in cis and trans polymers.

The analyses given previously[5] and above were substantially based on the models explored by Mark.[12,13] These models are now found to satisfactorily interpret experimental values of $\Delta\Gamma$ obtained with isotropic solvents within experimental error, provided that the values of statistical weight parameters adjusted to $\langle r^2 \rangle / n\bar{b}^2$ are combined with Clément and Bothorel's set[32] of anisotropic bond polarizabilities. However, Mark's treatments contain an oversimplified account of steric effects involved in some combinations of rotational states of bonds $i - 1$, i, and $i + 1$, in particular for PIP, as was pointed out by Flory.[26] We wish to briefly discuss these steric effects and their consequences on conformational features.

For PIP we calculated interatomic distances for the exhaustive combinations of rotational states of bonds $i - 1$, i, and $i + 1$ (see Figure 3). Of these, all those which are thought to cause medium or severe steric hindrances, as well as some reference ones, are given in Table X. Here steric hindrances were judged as usual from the comparison of interatomic distances with sums of van der Waals radii of relevant atom pairs (1.7 and 1.2 Å for the carbon and hydrogen atoms, respectively.[33])

As can be seen, severe steric interactions are exclusively related to the GS (or $G'S'$) and GC (or $G'C$) conformations of bonds i and $i + 1$. Those related to the GC conformation were accounted for through β in the foregoing scheme, but those related to the GS conformation were not. The incorporation of them through σ' would be inadequate because the GS' conformation

Table X. Interatomic distances for various rotational states of bonds $i-1$, i, and $i+1$, in PIP[a] (see also Figure 3)

	Rotational states			Atom pair	Distance (Å)
	$i-1$	i	$i+1$		
1	S			$H_{i-1}\ldots C_{i+1}$	2.88
2		T		$C_{i-1}\ldots C_{i+2}$	3.86
3		G		$C_{i-1}\ldots C_{i+2}$	3.01
4			S	$C_i\ldots C_s$	3.10
5			S	$C_i\ldots C_{i+3}$	3.59
6			C	$C_i\ldots C_s$	3.92
7			C	$C_i\ldots C_{i+3}$	2.87
8			C	$C_i\ldots H_{i+3}$	2.43
9		G	S	$C_{i-1}\ldots C_s$	2.80
10		G	S	$C_{i-1}\ldots H_s''$	2.11
11		G	C	$C_{i-1}\ldots H_{i+3}$	2.26
12	S	G	S	$H_{i-1}\ldots C_s$	2.12
13	S	G	S	$H_{i-1}\ldots H_s''$	1.17
14	S'	G	S	$C_{i-2}\ldots H_s''$	2.11
15	S	G	C	$H_{i-1}\ldots C_{i+3}$	2.28
16	S'	G	C	$C_{i-2}\ldots H_{i+3}$	2.11

[a] In addition to those given in Table V, the following parameters are used: the bond length of $C_{i+2} - C_s$ is 1.51 Å and that of every C–H is 1.1 Å. The tetrahedral symmetry is assumed for the methyl group. One of methyl hydrogens, H_s, is assumed to eclipse the double bond $C_{i+2} = C_{i+3}$.

does not involve more significant steric interactions than those in the TS (or TS') for PBE and PIP. We note that the GS conformation corresponds to the GG' conformation as in pentane, if $C_{i-1}C_iC_{i+1}C_{i+2}C_s$ is regarded as a skeleton. The $C_{i-1}\ldots C_s$ distance 2.8 Å is somewhat longer than the corresponding distance 2.6 Å in pentane. This is because an increase in the distance due to the larger (assumed) bond angle $\omega_a = 117.5°$ is more than offsetting a decrease due to the shorter bond length $b_{i+1} = b_s = 1.51$ Å. (Very recently a smaller bond angle $\omega_a = 113.6°$, which is com-

parable with 112° in pentane, was observed for a related compound.[34] Therefore steric interactions in the *GS* conformation are comparable with, or less severe than, those in the *GG'* of pentane, the latter conformation being usually discarded. As evidence, Shimanouchi and Abe[29] did not find the isomer corresponding to *GS* in their infrared study on 2-methyl-1-pentene. The foregoing considerations suggest that $\sigma \simeq 1$, being common for the four dienic polymers, and for *trans*-PIP P_1 in Eq. 5 would better be replaced by

$$P_1 = \lambda^{-1} \begin{bmatrix} 1 & 1 & \alpha^{1/2} \\ \sigma^{1/2}\xi & \sigma^{1/2} & (\alpha\sigma)^{1/2}\beta \\ \sigma^{1/2} & \sigma^{1/2}\xi & (\alpha\sigma)^{1/2}\beta \end{bmatrix} \quad (17)$$

where it is expected that $\xi \ll 1$. (Some three-bond interactions observed in Table X, No. 12 to 14, are neglected here. This assumption would be permissible because ξ is expected to be very small and the three-bond interactions are such as to become of no significance at $\xi = 0$.) Eq. 9 is now replaced[27] by

$$\left. \begin{array}{l} P_{1+} = \lambda^{-1} \begin{bmatrix} 2^{1/2} & \alpha^{1/2} \\ \sigma^{1/2}(\xi+1) & (2\alpha\sigma)^{1/2}\beta \end{bmatrix} \\[2ex] P_{1-} = \begin{bmatrix} 0 & 0 \\ \sigma^{1/2}(\xi-1) & 0 \end{bmatrix} \end{array} \right\} \quad (18)$$

The *C* and *S* conformations of bond $i + 1$

correspond to the *T* and *G'* conformations in butane if $C_i\ C_{i+1}\ C_{i+2}\ C_s$ is regarded as a skeleton. The $C_i \ldots C_s$ distance 3.1 Å in the *S* conformation is nearly equal to that in the *G* of butane. Therefore a repulsive energy of 0.5~0.8 kcal/mol is expected. This type of interaction is *a priori* absent in PBE. These results suggest that the value of α for *trans*-PIP, designated hereafter α', is larger than α for *trans*-PBE. As can be seen in Table X, the methyl group does not participate in the steric interactions involved in the *GC* conformation. This indicates that α should be common for *trans*-PBE and PIP, in accordance with Mark.[12]

The effect of suppressing the *GS* conformation for *cis*-PIP was examined. For $\alpha = 1$ (and $\gamma = \infty$[5]) we obtain the following results by using Clément and Bothorel's[32] set; ξ, $\langle r^2 \rangle/n\bar{b}^2$, $\Delta\Gamma$ (Å³); 1, 4.814, 4.735; 0.5, 4.584, 4.202; 0.25, 4.469, 3.939; 0, 4.354, 3.678. As is seen, both $\langle r^2 \rangle/n\bar{b}^2$ and $\Delta\Gamma$ are rather insensitive to ξ. The experimental value of $\langle r^2 \rangle/n\bar{b}^2 = 4.7$ is reproduced by $\xi = 0.75$ which yields $\langle r^2 \rangle/n\bar{b}^2 = 4.699$ and $\Delta\Gamma = 4.467$ Å³. This value of ξ should be subject to large uncertainty because a possible experimental error in $\langle r^2 \rangle/n\bar{b}^2$ results in an exaggerated error in ξ. The structure-geometric consideration given above indicates ξ to be much
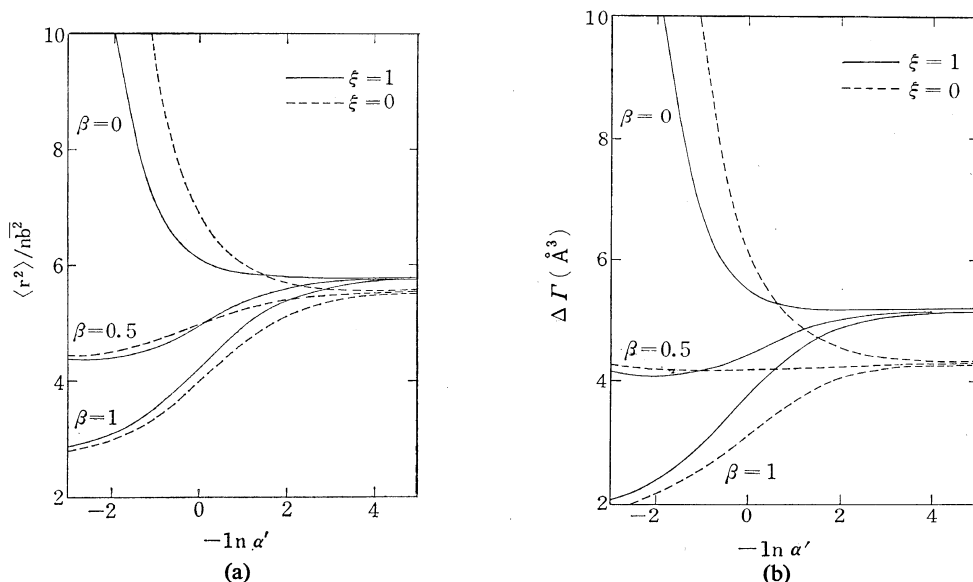

Figure 6. (a) $\langle r^2 \rangle/n\bar{b}^2$ and (b) $\Delta\Gamma$ *vs.* $-\ln\alpha'$, for the *trans*-PIP chain. Clément and Bothorel's set[32] of anisotropic bond polarizabilities is used.

smaller.

The effect of suppressing the *GS* conformation for *trans*-PIP is shown in Figures 6a and 6b, where solid curves correspond to $\xi = 1$ and broken curves to $\xi = 0$. The effect is medium or small, as in the case of *cis*-PIP. The number of parameters (ξ, α' and β), exceeds that of reliable experimental values, so that a unique determination of parameters is not possible. If we tentatively adopt $\xi = 0.75$ and $\beta = 0.1$, the experimental value $\langle r^2 \rangle / n\bar{b}^2 = 6.55$ is reproduced approximately by $\alpha' = 2.48$ ($E_{\alpha'} = -0.6$ kcal/mol at $T = 60°C$) which yields $\langle r^2 \rangle / n\bar{b}^2 = 6.48$ and $\Delta\Gamma = 6.04$ Å^3. If $\beta = 0.1$ is used for *trans*-PBE the adjusted value of α is $\alpha = 0.297$ ($E_\alpha = 0.9$ kcal/mole at $100°C$) which yields $\langle r^2 \rangle / n\bar{b}^2 = 5.82$ and $\Delta\Gamma = 6.13$ Å^3. The use of different values for α and α', *i.e.*, $\alpha' > \alpha$, is requisite for interpretation of the larger value of $\langle r^2 \rangle / n\bar{b}^2$ for *trans*-PIP. We have seen that the alternative interpretations for *cis*- and *trans*-PIP, based on ξ and α', give equally satisfactory results.

While the values of the statistical weight parameters given above do not appear unreasonable, they are, for the mostpart, only tentative. For a unique determination of them, more accurate experimental values of $\langle r^2 \rangle / n\bar{b}^2$ and, desirably, of $d\ln\langle r^2 \rangle / dT$, are needed. Careful studies of the rotational isomerism of appropriate model compounds also should provide valuable information to this end.

We have seen that, for all of the four dienic polymers, Clément and Bothorel's set[32] of anisotropic bond polarizabilities, combined with statistical weight parameters adjusted to experimental values of $\langle r^2 \rangle / n\bar{b}^2$, yield values of $\Delta\Gamma$ in satisfactory agreement with experimental values within possible experimental error and various approximations in theory. On the contrary, Denbigh's and Le Fevre's sets give less satisfactory results; Denbigh's set[30] yields lower values for the cis polymers and higher values for the trans polymers while Le Fevre's set[31] yields too low values for all. This result lends support to Clément and Bothorel's set.[32]

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