

## Thermoelastic Studies of Diene Polymers in Elongation and Compression\*

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**ABSTRACT:** Thermoelastic (stress—temperature) measurements have been carried out on networks of *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, and *trans*-1,4-polyisoprene under a variety of experimental conditions. Values of the temperature coefficient of the unperturbed dimensions of the network chains and the fraction  $f_e/f$  of the total force which is of energetic origin were calculated from these data and were found to be independent of cross-linking conditions, presence of diluent in the network during the stress—temperature measurements and type of deformation employed. The present results are found to be in good agreement with other experimental results reported for these polymers and their interpretation in terms of rotational isomeric state theory provides insight into the origin of the temperature dependence of the unperturbed dimensions of these chain molecules.

**KEY WORDS** Thermoelasticity / Stress—Temperature Measurements / Diene Polymers / Polybutadiene / Polyisoprene / Unperturbed Dimensions / Rotational Isomeric State Theory /

One of the most important quantities used to characterize the spatial configurations of a chain molecule is the temperature coefficient  $d \ln \langle r^2 \rangle_0 / dT$  of its unperturbed dimensions  $\langle r^2 \rangle_0$ .<sup>1</sup> A method which has proved to be particularly useful for the determination of this coefficient is the measurement of the temperature dependence of the force or stress exhibited by a deformed, amorphous network of the chains under investigation. Such “thermoelastic” studies have now been carried out on a wide variety of polymers,<sup>2</sup> and have contributed much to the understanding of chain configurations and their variation with changes in temperature.<sup>1,2</sup> Also calculable from

such measurements is the important fraction  $f_e/f$  of the elastic force which is of energetic rather than entropic origin.

The purpose of the present study was to obtain thermoelastic data, and values of  $d \ln \langle r^2 \rangle_0 / dT$  and  $f_e/f$  derived therefrom, for the diene polymers *cis*-1,4-polybutadiene (*cis*-PBD), *trans*-1,4-polybutadiene (*trans*-PBD), and *trans*-1,4-polyisoprene (*trans*-PIP). (*cis*-1,4-Polyisoprene, alias natural rubber, was not included here for investigation, since it has already been extensively studied by these techniques. It has been, in fact, the subject of more thermoelastic studies ( $\sim 20$ )<sup>2</sup> than any other polymer.) The required networks of these polymers were prepared under a variety of cross-linking conditions in order to determine the possible effect of variation in such conditions on  $d \ln \langle r^2 \rangle_0 / dT$  and  $f_e/f$ . For the same reason a variety of experimental conditions were used in the determination of the stress—temperature relationships. Some comparisons can be made

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between the results of the present study and those reported in the literature. Of the polymers studied here, however, only the *cis*-PBD has been studied previously in detail;<sup>2</sup> previous results on *trans*-PIP<sup>3</sup> are very limited, and are entirely lacking in the case of *trans*-PBD. Also of importance is the comparison of the experimental results with theoretical results calculated on the basis of rotational isomeric state models of these chain molecules.<sup>4-10</sup> Such comparisons directly yield information on the configurations of the polymer chains, and, most importantly, the transitions between configurations in response to changes in temperature.<sup>1,2</sup>

### EXPERIMENTAL

Three series of *cis*-PBD networks were prepared from two polymer samples<sup>11</sup> which were at least 94-% *cis*-1,4 in stereochemical structure on the basis of analysis<sup>12</sup> of their infrared spectra. Undiluted polymer was used for two of these series; the first was obtained using 0.1–1.5-wt% dicumyl peroxide (DCP) at 155°C for 6 hr,<sup>13</sup> and the second by means of  $\beta$ -radiation (40–80 Mrad) in the vicinity of room temperature. The third series<sup>14</sup> was prepared from a solution of the *cis*-PBD in toluene which had a volume fraction  $\phi_2$  of polymer of 0.26; cross-linking was brought about in this case by  $\gamma$ -radiation (11 Mrad) at 25°C. Approximately 1 wt% or less of the antioxidant *N*-phenyl-2-naphthylamine (NPNA) was incorporated into some of these networks.<sup>13,14</sup>

The sample<sup>11</sup> of *trans*-PBD employed was essentially 100-% *trans*-1,4 on the basis of its infrared spectrum.<sup>12</sup> A mixture of equal weights of polymer and NPNA were milled together at 150°C, and the polymer in the resulting solution was cross-linked using approximately 15 parts of DCP per 100 parts of polymer at the same temperature for 6 hr. The NPNA was left in the network to act as both diluent and antioxidant during the stress–temperature measurements.

The *trans*-PIP sample<sup>11</sup> was also essentially 100-% *trans*-1,4 on the basis of infrared analysis.<sup>15</sup> One series of networks was prepared using 2-wt% DCP at 140°C, and another using  $\beta$ -radiation (70–90 Mrad) at room temperature.<sup>13</sup> Approximately 1-wt% of NPNA was incorporated into several<sup>13</sup> of these networks in order to

minimize oxidative degradation.

Additional details regarding the preparation of these networks may be found elsewhere.<sup>13,14</sup> Those networks with the greatest thermal stability were chosen for the force–temperature measurements; they are described in the first two columns of Table I.

The stress–temperature measurements were carried out using techniques described in detail elsewhere.<sup>13,14,16,17</sup> A variety of experimental conditions were employed. Networks were studied both swollen with a constant amount of nonvolatile diluent and in the unswollen state, in both elongation<sup>13</sup> and compression,<sup>14</sup> and at both constant length  $L$ <sup>13</sup> and constant deformation  $\alpha$ .<sup>14</sup> These details, and also the temperature ranges covered, are given in column three of the Table; the values of the deformation employed are given in the following column. For the networks in elongation, the sample was held at constant length and the force or stress recorded at a number of temperatures in the range cited.<sup>13</sup> In the case of the compression measurements, on the *cis*-PBD, however, a more elaborate scheme was employed. The entire stress–strain isotherm was obtained at each temperature of interest and was represented by a linear relationship determined by least squares analysis. The dependence of stress on temperature at constant  $\alpha$  was then obtained from these straight lines by interpolations and limited extrapolations.<sup>14,17</sup>

The data thus obtained were checked for reversibility by either remeasuring the entire force–temperature relationship at the same deformation to determine whether or not the same fractional change in force with temperature was obtained,<sup>13</sup> or by simply remeasuring the force at a few selected values of the deformation at each temperature. Force–temperature coefficients thus obtained were generally found to be highly reproducible. In the case of the *trans*-PBD, however, the results were only approximately reproducible because of network degradation.<sup>13</sup> These measurements were made even more tentative by the fact that only a relatively small range of temperature could be covered. Degradation became excessive above 110°C and network crystallization precluded reliable measurements below 90°C.<sup>13</sup>

Thermal expansion coefficients  $\beta = (\partial \ln V / \partial T)_p$

Table I. Experimental conditions and thermoelastic results

Polymer	Cross-linking conditions	$f-T$ conditions	$\alpha$	$-10^3 \left[ \frac{\partial \ln \langle f^* \rangle / T}{\partial T} \right]_p$	$f_0/f$	$10^3 \frac{d \ln \langle r^2 \rangle_0}{dT}$
<i>cis</i> -1,4-Polybutadiene	Undil., peroxide cure, 155°C	Unswollen, elong., const $L$ , 50–90°C	1.25	1.06	0.12	0.35
	"	"	1.35	0.71	0.08	0.24
	Undil., $\beta$ -rad., room temp.	"	1.34	0.84	0.12	0.36
	In soln., <sup>a</sup> $\gamma$ -rad., 25°C	Unswollen, comp., const $\alpha$ , 25–65°C	0.95	0.20	0.14	0.43
	"	"	0.90	0.23	0.14	0.45
	"	"	0.85	0.25	0.15	0.48
	"	Swollen, <sup>b</sup> comp., const $\alpha$ , 25–65°C	0.90	0.27	0.13	0.41
	"	"	0.85	0.30	0.14	0.44
	"	"	0.80	0.33	0.15	0.47
			0.75	0.36	0.16	0.51
				Av	0.13	0.41
					( $\pm 0.02$ )	( $\pm 0.06$ )
<i>trans</i> -1,4-Polybutadiene	In soln., <sup>c</sup> peroxide cure, 150°C	Swollen, <sup>c</sup> elong., const $L$ , 90–110°C	1.27	0.33	-0.13	-0.34
	"	"	1.34	-0.35	-0.32	-0.85
	"	"	1.37	0.00	-0.17	-0.45
				Av	-0.21	-0.55
					( $\pm 0.08$ )	( $\pm 0.20$ )
<i>trans</i> -1,4-Polyisoprene	Undil., peroxide cure, 140°C	Unswollen, elong., const $L$ , 40–90°C	1.36	0.11	-0.12	-0.35
	"	"	1.40	0.05	-0.12	-0.35
	"	"	1.72	-0.47	-0.22	-0.64
	Undil., $\beta$ -rad., room temp.	"	1.19	0.66	-0.12	-0.35
	"	"	1.20	0.91	-0.01	-0.04
	"	"	1.26	0.47	-0.07	-0.22
	"	"	1.31	0.24	-0.10	-0.31
			Av	-0.11	-0.32	
					( $\pm 0.04$ )	( $\pm 0.11$ )

<sup>a</sup> Solvent was toluene, and volume fraction of polymer was  $\phi_2=0.26$ .

<sup>b</sup> Diluent was 1-chloronaphthalene, and volume fraction of polymer was  $v_2=0.52$ .

<sup>c</sup> Solvent and diluent were *N*-phenyl-2-naphthylamine, and volume fraction of polymer was  $\phi_2=v_2\cong 0.5$ .

were determined by dilatometry over the appropriate temperature ranges. The values obtained for the unswollen *cis*-PBD and the *cis*-PBD swollen with 1-chloronaphthalene were 0.683 and  $0.465 \times 10^{-3} \text{ K}^{-1}$ , respectively.<sup>14</sup> For the swollen *trans*-PBD networks and the unswollen *trans*-PIP networks, the values were 0.70 and  $0.69 \times 10^{-3} \text{ K}^{-1}$ , respectively.<sup>13</sup>

The cross-sectional area  $A^*$  of the cylindrical *cis*-PBD sample to be used in the compression measurements was determined using a micrometer; this sample had a diameter of 1.47 cm in the

unswollen, undeformed state at 25°C. The samples studied in elongation had rectangular cross-sections, the areas of which had regrettably not been recorded because  $f_0/f$  and  $d \ln \langle r^2 \rangle_0 / dT$  are independent of  $A^*$ . The reasonable estimate  $A^*=0.07 \text{ cm}^2$  was used for each of these samples.

## RESULTS AND DISCUSSION

Values of the force  $f$ , cross-sectional area  $A^*$ , volume fraction of polymer in the network  $v_2$ , and deformation  $\alpha$  were used to calculate values

of the "reduced force"  $[f^*]$  defined by

$$[f^*] = fv_2^{1/3}/A^*(\alpha - \alpha^{-2}) \quad (1)$$

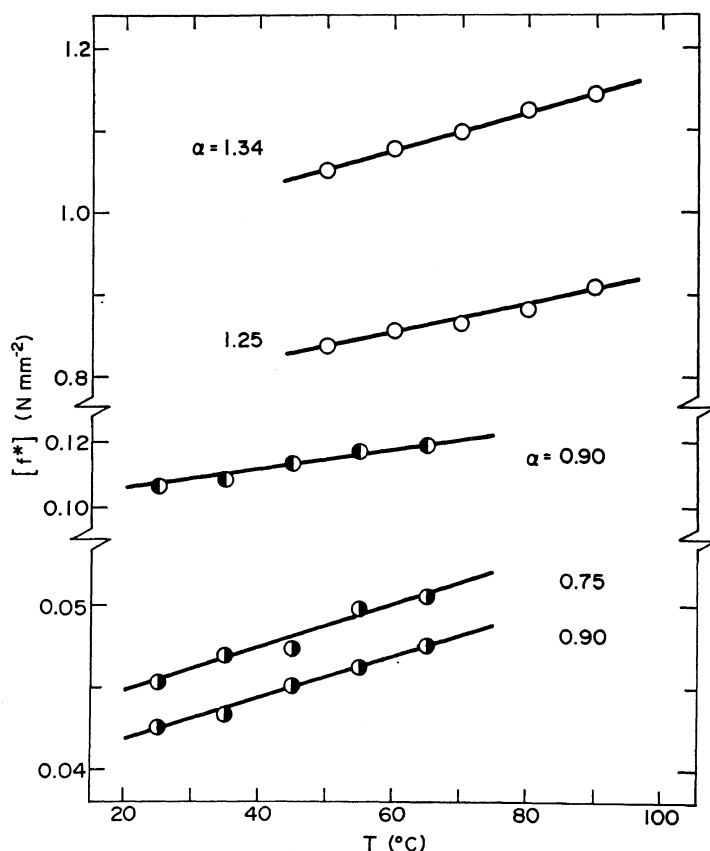
In the case of the compression measurements, sufficient data were available to obtain stress-strain isotherms at 25, 35, 45, 55, and 65°C. These isotherms were represented by the semi-empirical equation of Mooney and Rivlin<sup>18</sup>

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (2)$$

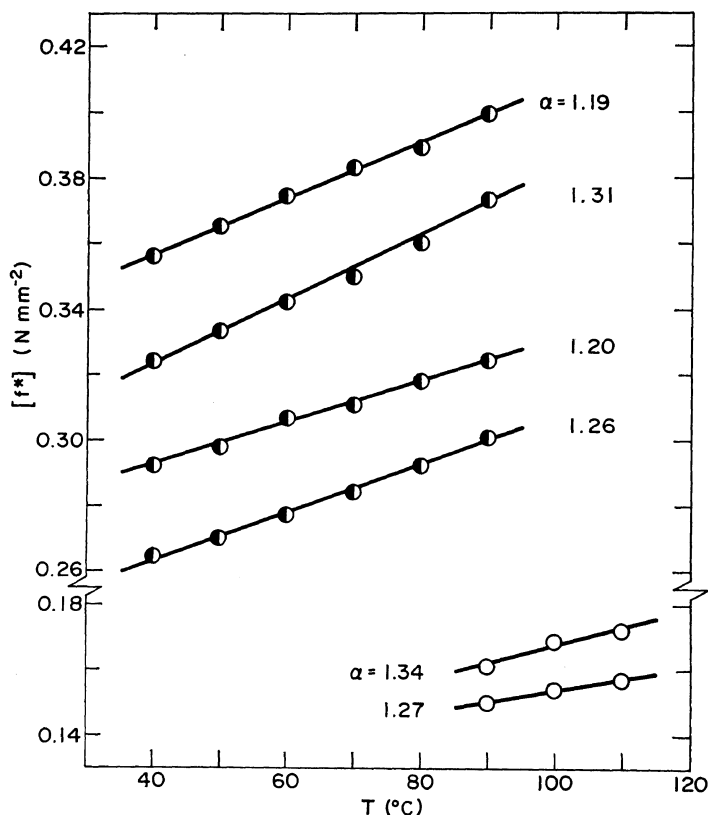
Values of the constant  $2C_2$ , which represents a measure of the deviation of the observed isotherms from the form indicated by the statistical theories of rubberlike elasticity,<sup>19</sup> were found to be  $-0.010(\pm 0.001)$  and  $0.014(\pm 0.002)Nmm^{-2}$

for the unswollen and swollen *cis*-PBD networks, respectively.<sup>14,20</sup> There was no evident trend of  $2C_2$  with temperature in either case. These values of  $2C_2$  are very much smaller than the values generally observed for networks in elongation, in agreement with previous results obtained from compression measurements.<sup>21</sup>

The reduced force was plotted against the temperature for each sample, at each value of the deformation investigated. Linear relationships were obtained and the straight line best representing a given set of stress-temperature data was located by the method of least squares; typical results are shown in Figures 1 and 2.<sup>22</sup> These data were then used to calculate values



**Figure 1.** The reduced force shown as a function of temperature for *cis*-PBD networks. The open circles locate typical results obtained on unswollen networks in elongation at constant length.<sup>13</sup> Half-filled circles correspond to representative results<sup>14</sup> in compression at constant deformation  $\alpha = L/L_i$ ; left-filled circles pertain to unswollen networks and right-filled circles to a network swollen with the nonvolatile diluent 1-chloronaphthalene. In this and the following figure, each curve is labelled with the appropriate value of the deformation.



**Figure 2.** The reduced force shown as a function of temperature for networks of *trans*-PBD and *trans*-PIP in elongation at constant length. Open circles locate typical results obtained on *trans*-PBD networks swollen with the antioxidant *N*-phenyl-2-naphthylamine; the half-filled circles pertain to unswollen networks of *trans*-PIP.

of the coefficient  $[\partial \ln ([f^*]/T)/\partial T]_p$ , where  $T$  is the absolute temperature. The results, which pertain to constant  $L$  in the case of elongation and to constant  $\alpha$  in the case of compression, are shown in column five of Table I. Values of  $f_e/f$  and  $d \ln \langle r^2 \rangle_0/dT$  were then calculated from the equations<sup>23</sup>

$$f_e/f = T d \ln \langle r^2 \rangle_0/dT \quad (3)$$

$$f_e/f = -T [\partial \ln ([f^*]/T)/\partial T]_{p,L} - \beta T/(\alpha^3 - 1) \quad (4)$$

$$f_e/f = -T [\partial \ln ([f^*]/T)/\partial T]_{p,\alpha} + \beta T/3 \quad (5)$$

and are given in the last two columns of the Table. It should be noted that the results shown indicate that these two important quantities do not depend significantly on the conditions used to prepare the networks, the presence of diluent in the network during the stress—temperature

determinations, nor the type of deformation employed. This is in agreement with conclusions reached upon analysis of thermoelastic data on a number of other polymer systems.<sup>2,16</sup>

Since  $f_e/f$  and  $d \ln \langle r^2 \rangle_0/dT$  embody equivalent information (as is shown in eq 3), only the latter quantity will be discussed in detail. The value of  $10^3 d \ln \langle r^2 \rangle_0/dT$  obtained for *cis*-PBD from these tabulated results is  $0.41(\pm 0.06)K^{-1}$ ; results from seven additional experiments in elongation, of lower reversibility and therefore not described in Table I, gave  $0.44(\pm 0.06)K^{-1}$ . These results are in good agreement with the value  $0.39(\pm 0.10)K^{-1}$  obtained by averaging the results reported in a number of earlier studies.<sup>2</sup> The result  $10^3 d \ln \langle r^2 \rangle_0/dT = -0.55(\pm 0.20)K^{-1}$  obtained for *trans*-PBD must be regarded as very tentative for reasons already mentioned; it is nonetheless

presented here as a preliminary result since no other thermoelastic results are available for this polymer. In the case of the *trans*-PIP, the result  $10^3 d \ln \langle r^2 \rangle_0 / dT = -0.32 (\pm 0.11) K^{-1}$  is in very good agreement with the value  $-0.29 (\pm 0.11) K^{-1}$  obtained by Gent and Kuan,<sup>3</sup> also on unswollen *trans*-PIP networks but employing torsion as the deformation. This agreement is of considerable importance because of its relevance to the question of the alleged existence<sup>24</sup> of intermolecularly ordered regions in amorphous polymers. One would reasonably expect any such ordering, if present, to respond differently to elongation than it would to torsion. The observed agreement between the values of  $d \ln \langle r^2 \rangle_0 / dT$  obtained using these two very different types of deformation therefore constitutes evidence against the presence of such ordered domains in polymers in the amorphous state.

Results of rotational isomeric state calculations<sup>4-10</sup> can be used to give a simple physical picture of the molecular origin of the temperature dependence of the unperturbed dimensions of these diene chains. In the case of *cis*-PBD,  $\langle r^2 \rangle_0$  increases with increasing temperature because the lowest energy conformations about  $CH_2-CH=CH-CH_2$  bond pairs are  $\pm 60^\circ$ ,  $\pm 60^\circ$  and  $\mp 60^\circ$ ,  $\pm 60^\circ$  states, which are relatively compact. Increase in temperature thus increases the population of less compact rotational states. In the case of *trans*-PBD and *trans*-PIP, however, extended  $180^\circ$ ,  $0^\circ$  states about  $CH-CH_2-CH_2$  bond pairs are of lower energy than the very compact  $180^\circ$ ,  $\pm 120^\circ$  states. For these *trans* diene polymers, therefore, increase in temperature decreases  $\langle r^2 \rangle_0$ , again in agreement with experiment.

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20. In order to facilitate comparison of these results with others in the literature in different units, it may be helpful to point out that  $1 Nmm^{-2} = 1 MNm^{-2} = 10.20 kg cm^{-2}$ .
21. Some typical studies of polymer networks in compression are cited in ref 17.
22. As is now customary (ref 2), a specific (constant) value of  $\alpha$  is employed to designate even those curves corresponding to data at constant length, and is used to calculate a single value of the correction term  $\beta T / (\alpha^3 - 1)$  in eq 4 for each such curve. The effect of this simplification is known to be negligible (ref 16). Also, utiliza-

tion of the reduced force  $[f^*] = f v_2^{1/3} / A^*(\alpha - \alpha^{-2})$  in such plots facilitates comparisons between different stress—temperature curves; use of a constant value of  $\alpha$  here is totally inconsequential since it is only the *fractional* change in this quantity with temperature which appears in

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