

Characterization of Two Polypentadienes of Differing Tacticity by Physical Methods

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Synopsis

The preparation of isotactic and syndiotactic 1,4-polypentadienes with a *cis* content of at least 70%–75% using $i\text{-Bu}_2\text{AlH/Ti}(i\text{-OPr})_4$ and $\text{AlEtCl}_2/\text{thiophene/Co}(\text{acetylacetonate})_2$ catalysts, respectively, is reported. Physical characterization of the vulcanizates, prepared by a common recipe, involving infrared analysis, DTA, simple stress-strain and swelling measurements, and dynamic mechanical measurements over a frequency range of 2 decades and temperature range of -60°C to $+20^\circ\text{C}$ indicated that no isomerization had taken place during vulcanization and that stereoregularity of the polymer chains affected the resultant cure: the isotactic form was found to have a greater crosslink density than the syndiotactic form. Master curves covering an extended frequency range were constructed from the reduced dynamic mechanical data and the calculated quantities—thermal expansion coefficients of free volume and the fractional free volumes at the glass transition temperatures—agree with the accepted values. Glass transition temperatures of the isotactic and syndiotactic polymers are -37°C and -42°C , respectively, and, for their vulcanizates, -33°C and -40°C , respectively.

INTRODUCTION

At the present time, four polymers of 1,3-pentadiene are known which possess a fairly high degree of stereoregularity. These are isotactic *trans*-1,4-polypentadiene,¹ syndiotactic *trans*-1,2-polypentadiene,² isotactic *cis*-1,4-polypentadiene,³ and syndiotactic *cis*-1,4-polypentadiene.⁴ Apart from polymer characterization by infrared,⁵ nuclear magnetic resonance,⁵ and x-ray analysis, few physical property data on these polymers have appeared. Some vulcanizate properties, e.g., tensile strengths, percentage elongations, and moduli, on isolated polymers have appeared in patents^{6,7} but no fundamental study has been reported. This paper describes a physical characterization, involving simple tensile stress-strain, swelling, and dynamic mechanical techniques, on isotactic and syndiotactic 1,4-polypentadiene vulcanizates containing a minimum of 70%–75% *cis* units.

EXPERIMENTAL

Polymer Preparation

Isotactic 1,4-Polypentadiene with More Than 70% *cis* Content. Four-ounce glass bottles were charged with benzene (20.4 g), diisobutylhydrido-

aluminum (0.56 g), and tetraisopropoxytitanium (0.22 g) (an Al/Ti ratio of 5). After 1 hr, portions of premix, which had been dried by passage through silica gel, containing 1,3-pentadiene (8.2 g) (96% *trans* isomer, 3% *cis* isomer, 1% isoprene) in benzene (45.4 g), were added to the preformed catalyst. The resulting mixtures were stirred for 25 hr.

Polymerization was terminated by pouring the cements into a large excess of methanol containing an antioxidant. The polymer was dried under vacuum. A sufficient number of bottles, each giving 6.5 g of isolated polymer having a DSV of 3.0, a Mooney viscosity (ML-4) of 76, and 6% gel, were run in order to give enough polymer to carry out the physical measurements. Infrared analysis indicated better than 70% *cis* units, and nuclear magnetic resonance indicated better than 90% 1,4-units.

Syndiotactic *cis*-1,4-Polyentadiene with More Than 75% *cis* Content. Premixes comprising 1,3-pentadiene (17.3 wt-%) (70% *trans* isomer, 30% *cis* isomer) in benzene were dried over silica gel and portions containing 5.3 g pentadiene were placed into 4-oz glass bottles equipped with self-sealing rubber gaskets. A suspension of cobalt diacetylacetonate (6.65×10^{-6} moles) in benzene (0.05 ml) was added to the bottles by means of a hypodermic syringe, followed by thiophene (0.15 ml) and, after 15 min, dichloroethylaluminum (1.75×10^{-3} moles) in benzene (1.2 ml). Polymerization was terminated after 20 hr by the addition of a solution containing antioxidant, 0.3 ml methanol, and 0.7 ml benzene. The polymer was isolated by coagulation in excess methanol and dried under vacuum overnight. Again a sufficient number of bottles, each giving 5.3 g of isolated solid polymer having a DSV of 1.4, a Mooney viscosity (ML-4) of 14, and 5.2% gel, were run in order to obtain enough polymer to carry out the physical measurements. Infrared analysis indicated at least 75% *cis* units and nuclear magnetic resonance showed at least 85% 1,4-units in the polymer. The *cis/trans* isomer ratio is known not to influence the polymerization appreciably when the percentage of *cis* isomer is in the order of or below that used in the present preparation.⁸

For reasons already reported,⁹ the infrared analyses given in this paper must be considered approximate and conservative, since the values of the adsorption coefficients are not precisely known.

Vulcanization of Polymer Samples

The polymer vulcanizates, using reprecipitated polymer, were prepared on a warm mill according to the recipe and conditions listed in Table I.

Infrared analysis on the pure gums indicated that no isomerization occurred during the vulcanization process so that the vulcanizates are essentially copolymers of 70%–75% *cis*-1,4 units and 30%–25% *trans*-1,4 units for the isotactic and syndiotactic forms, respectively.

Apparatus and Procedure

Characterization of the vulcanizates was via differential thermal analysis (du Pont 900, for glass transition temperature estimation), simple

TABLE I
Mix Recipe and Vulcanization Conditions^a

Ingredient	Parts by weight
Polymer	100.0
Sulfur	2.0
Zinc oxide	5.0
Stearic acid	2.0
Accelerator ^b	0.5
Antioxidant ^c	1.0

^a Vulcanization 30 min at 143.5°C.

^b Tetramethylenethiuram disulfide.

^c Mixture of aryl-*p*-phenylenediamine antioxidants.

tensile stress-strain measurements, equilibrium swelling measurements in benzene at 30°C, and dynamic mechanical measurements.

The dynamic storage moduli E' and the dynamic loss moduli E'' of the vulcanizates were determined by using a simple forced vibration apparatus whereby small polymer beams ($4 \times 0.5 \times 0.2$ cm), mounted as cantilevers, are caused to vibrate at small strains (~ 0.1 cm) over a 2-decade frequency range (0.1 to 10 Hz). Measurements were taken over the temperature range -60°C to $+20^\circ\text{C}$. The dynamic functions were calculated from the following expressions:

$$E' = \frac{F}{A_d} \cdot \frac{l^3}{bd^3} \frac{\cos\phi - A}{(\cos\phi - A)^2 + \sin^2\phi} \quad (1)$$

$$E'' = \frac{F}{A_d} \cdot \frac{l^3}{bd^3} \frac{\sin\phi}{(\cos\phi - A)^2 + \sin^2\phi} \quad (2)$$

where F is the measured force at the nondriven end of the beam sample, A_d is the driving amplitude, A is the nondriven end-to-driven end amplitude ratio, ϕ is the lag angle between the two ends of the beam sample, and l , b , and d are the sample length, width, and thickness, respectively. A detailed analysis of the derivation of eqs. (1) and (2) has already been given.¹⁰

RESULTS AND DISCUSSION

Figure 1 shows the characterization of the vulcanizates at room temperature via plots of the Mooney-Rivlin equation in the form

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + C_2/\lambda. \quad (3)$$

The intercepts and slopes of this relation represent the constants C_1 and C_2 ; σ is the tensile stress required to extend the test piece to various extension ratios λ . The average molecular weight between crosslinks, M_c , was calculated from swelling measurements using

$$2C_1 = \frac{\rho RT}{M_c} V_r^{0.3} \quad (4)$$

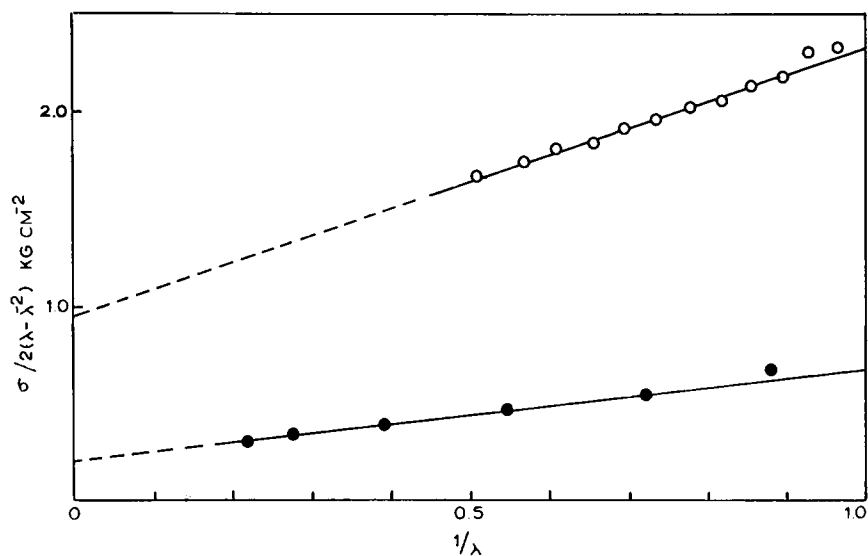


Fig. 1. Mooney-Rivlin plots for isotactic and syndiotactic *cis*-1,3-polybutadiene vulcanizates: (○) isotactic; (●) syndiotactic.

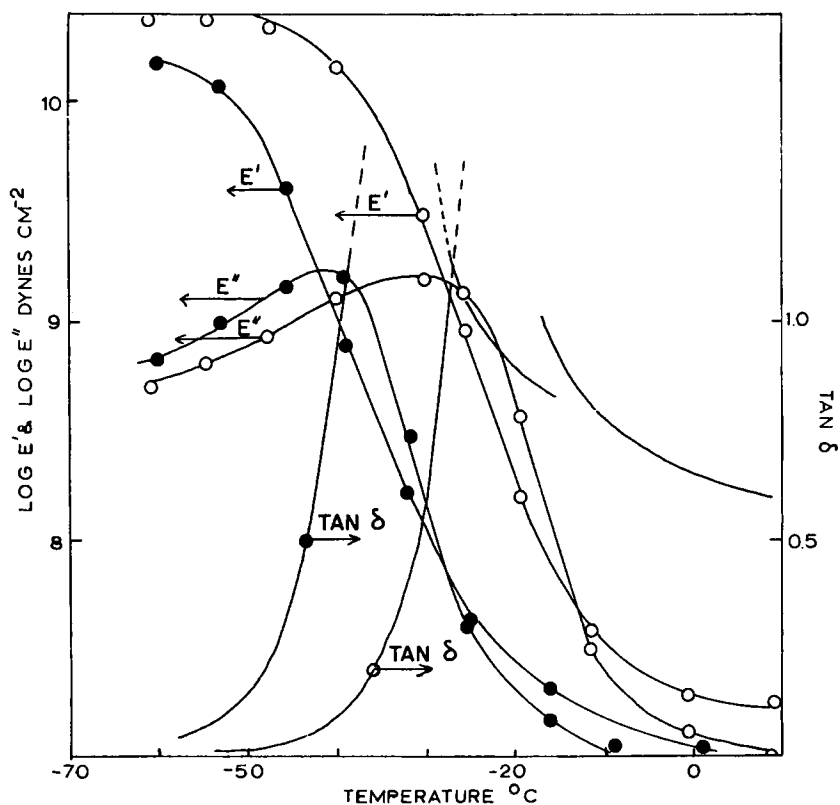


Fig. 2. Dynamic mechanical data for isotactic and syndiotactic *cis*-1,4-polybutadiene vulcanizates at 1 Hz: (○) isotactic; (●) syndiotactic.

TABLE II
Summary of Experimental Data

	Syndiotactic	Isotactic
T_g , °C (unvulcanized)	-42	-37
T_g , °C (vulcanizate)	-40	-33
C_1 , kg cm ⁻²	0.22	0.96
C_2 , kg cm ⁻²	0.5	1.33
V_r	0.10	0.19
χ_1	0.54	0.59
M_e	28000	6650
c_1^0	11.63	18.75
c_2^0	38.90	123.75
$c_1^0 c_2^0$	453.34	2320.31
c_1^g	10.14	17.68
c_2^g	45.16	131.35
$c_1^g c_2^g$	457.92	2322.27

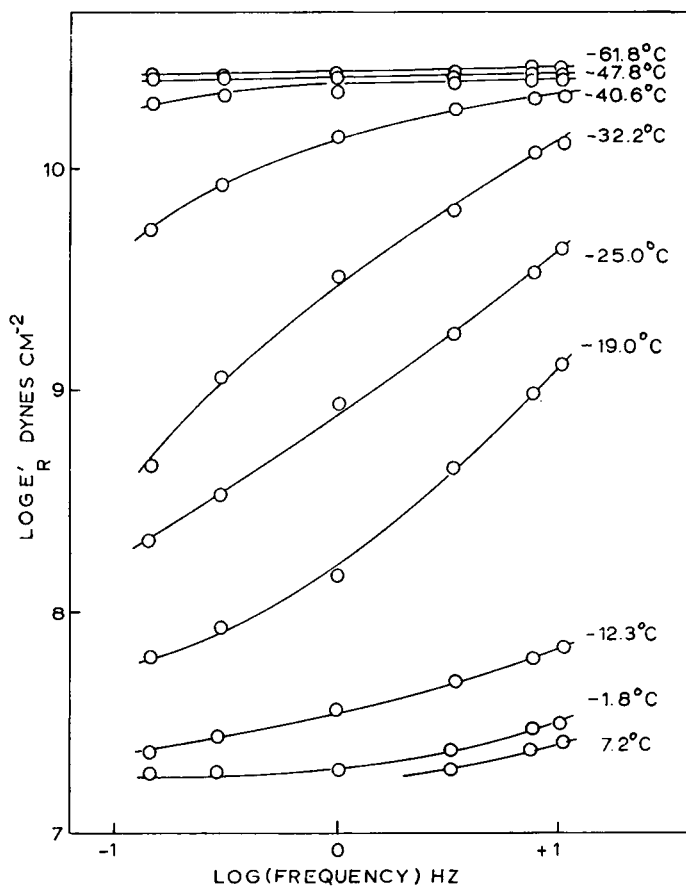


Fig. 3. Storage modulus-frequency data for isotactic *cis*-1,4-poly-pentadiene vulcanizate.

where V_r is the volume fraction of rubber in the swollen gel at 30°C. The Flory-Huggins relation¹¹ between M_c and V_r was used to calculate the polymer-solvent interaction coefficient χ_1 .

The above data are summarized in Table II. The molecular weight between crosslinks is substantially higher for the syndiotactic form ($M_c = 28000$) than for the isotactic form ($M_c = 6650$), and the C_1 value for the

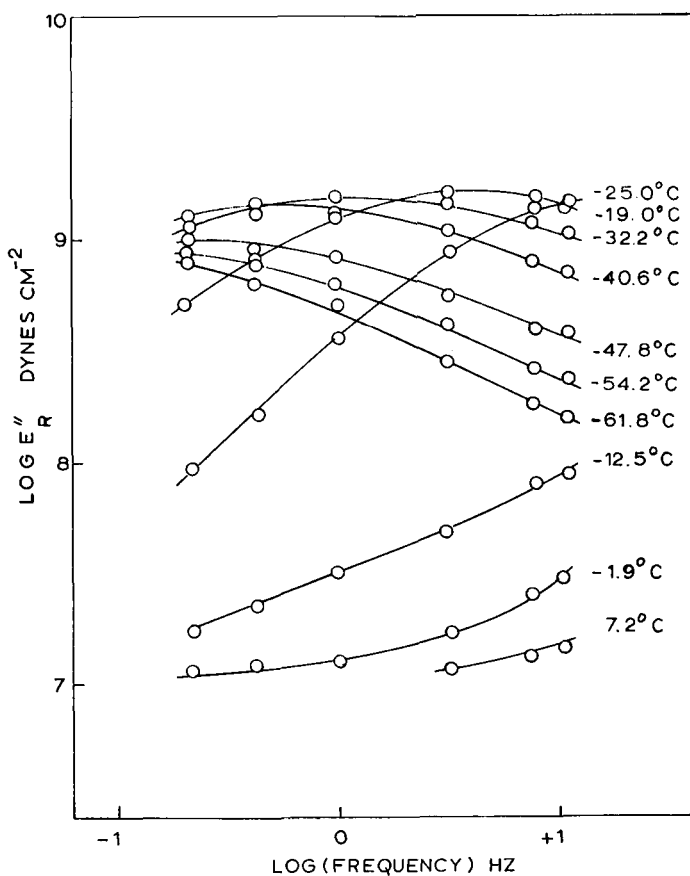


Fig. 4. Loss modulus-frequency data for isotactic *cis*-1,4-polybutadiene vulcanizate:

isotactic form is substantially larger than the value for the syndiotactic form. These values indicate that the isotactic form is more highly cross-linked than is the syndiotactic form.

The differences in the physical properties of the two vulcanizates can be discussed via the tacticity of their high *cis*-1,4 content, because the *trans*-1,4 content (25% and 30%) is similar in each vulcanizate and also because the present catalyst system is not known to yield stereospecific *trans*-1,4-polybutadienes. It is therefore assumed that the *trans*-1,4 content is atactic and randomly distributed throughout the chains since no crystal-

linity, normally associated with the *trans*-1,4 structure, was observed in these polymers.

A summary of the dynamic mechanical data for both the isotactic and syndiotactic forms, E' , E'' , and the loss tangent $\delta = E''/E'$ at 1 Hz plotted in the temperature plan is shown in Figure 2. Both sets of data exhibit a relaxation process denoted by maxima in E'' and $\tan \delta$ at temperatures

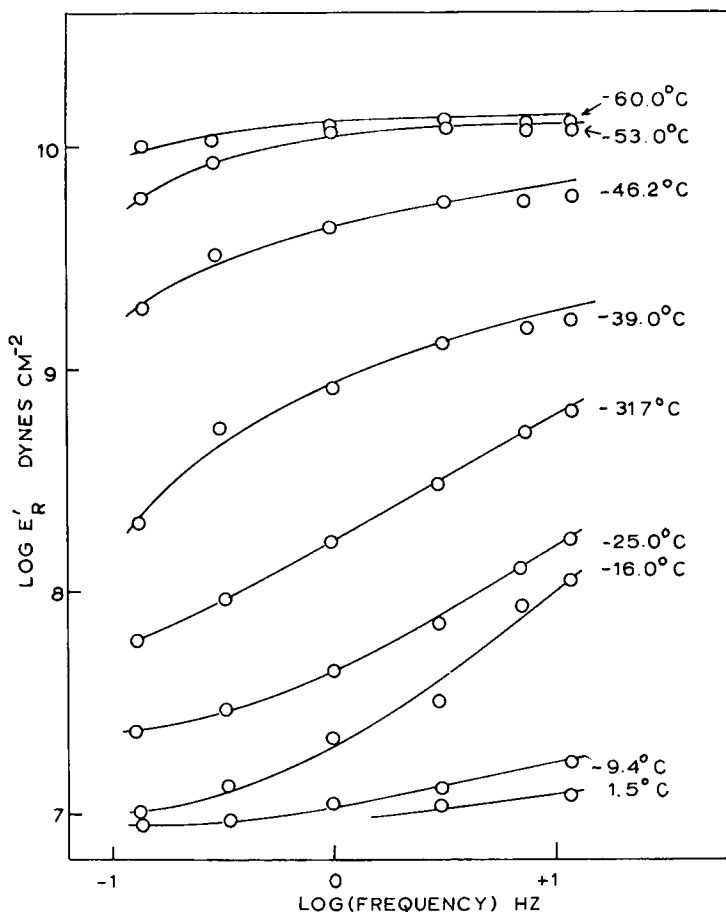


Fig. 5. Storage modulus-frequency data for syndiotactic *cis*-1,4-polypentadiene vulcanizate.

only slightly higher than the measured glass transition temperature T_g . The accompanying 3-decade decrease of the storage moduli in these temperature regions suggests that this process is associated with the glass-rubber transition.

The dynamic mechanical data for the isotactic vulcanizate lie as much as 10°C higher than the corresponding data for the syndiotactic polymer; also the modulus E' in the region above the glass transition is higher for the

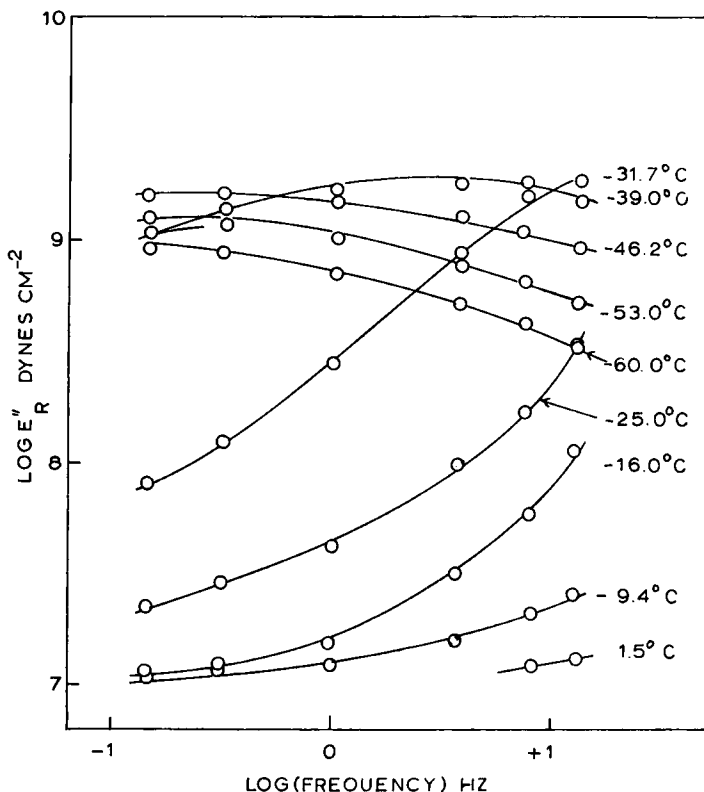


Fig. 6. Loss modulus–frequency data for syndiotactic *cis*-1,4-polybutadiene vulcanizate.

isotactic vulcanizate. The relative increase in the glass transition temperature after vulcanization is also higher for the isotactic form, being 4° , whereas the increase for the syndiotactic form is 2° . These data also suggest a higher degree of crosslinking in the isotactic vulcanizate, as was already indicated by the levels of the C_1 constants and the M_c values, thus lending further support to the hypothesis that the isotactic form is more susceptible to vulcanization than is the syndiotactic form.

Characterization is further extended by shifting the log storage and log loss moduli curves plotted in the frequency plane, Figures 3 and 4 for the isotactic form and Figures 5 and 6 for the syndiotactic form, to reference temperatures of -40.6°C and -46.2°C , respectively (Figs. 7 and 8) by the method of reduced variables.¹² The horizontal shift factor, $\log a_T$, was fitted to the WLF equation, as follows:

$$-\frac{(T - T_0)}{\log a_T} = \frac{c_2^0}{c_1^0} + \frac{(T - T_0)}{c_1^0} \quad (5)$$

where c_1^0 and c_2^0 are experimentally determined constants. This factor is shown by the straight lines in Figure 9. The values for the constants for the

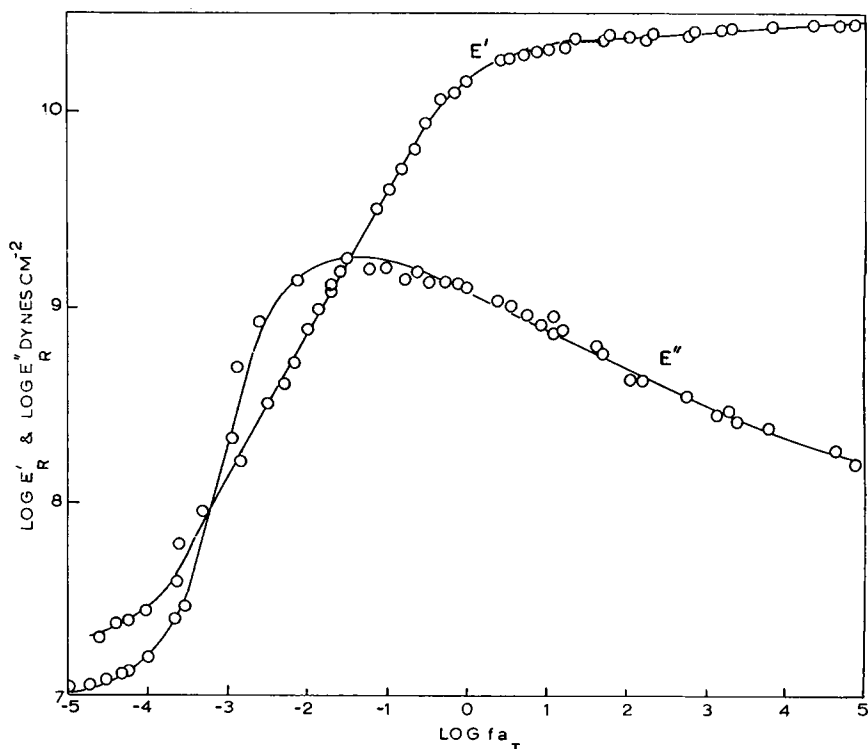


Fig. 7. Reduced storage and loss moduli master curves for isotactic *cis*-1,4-polybutadiene vulcanizate at -40.6°C .

isotactic form at -40.6°C and the syndiotactic form at -46.2°C are $c_1^0 = 18.75$, $c_2^0 = 123.75$ and $c_1^0 = 11.63$, $c_2^0 = 38.98$, respectively. These values were used to calculate the WLF coefficients c_1^g and c_2^g corresponding to glass transition temperatures of $T_g = -33^{\circ}\text{C}$ for the isotactic form and $T_g = -40^{\circ}\text{C}$ for the syndiotactic form. The coefficients were found to be $c_1^g = 17.68$, $c_2^g = 131.35$ for the isotactic form and, for the syndiotactic form, $c_1^g = 10.14$, $c_2^g = 45.16$.

The theoretical expansion coefficients of free volume α_f and the fractional free volume at the glass transition temperature f_g were determined by comparing the coefficients of the WLF (T_g) equation [eq. (5)] with those of the following equation¹²:

$$\log a_T = \frac{(-B/2.303 f_g)(T - T_g)}{(f_g/\alpha_f) + (T - T_g)} \quad (6)$$

so that

$$f_g = B/(2.303 c_1^g)$$

and

$$\alpha_f = B/(2.303 c_1^g c_2^g)$$

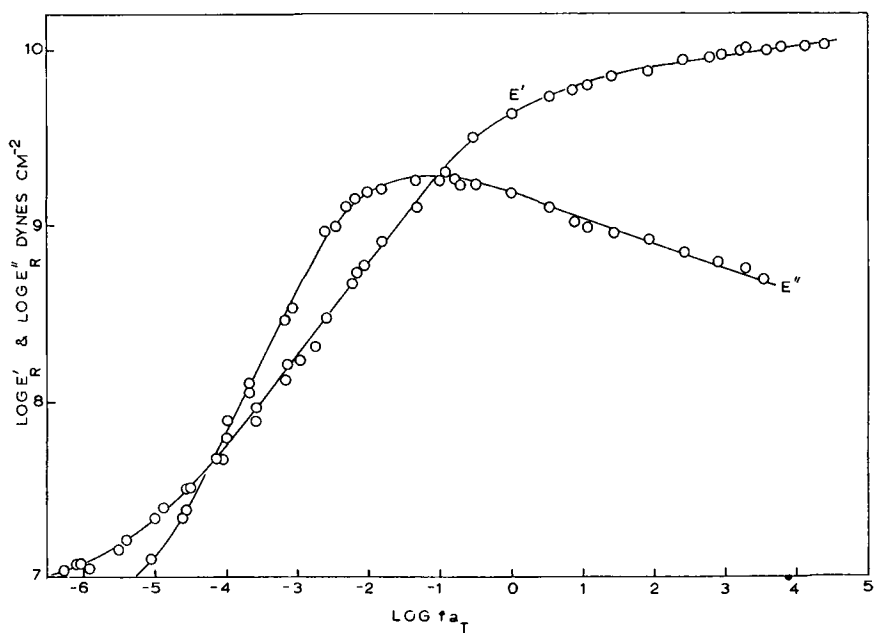


Fig. 8. Reduced storage and loss moduli master curves for syndiotactic *cis*-1,4-poly-pentadiene vulcanizate at -46.2°C .

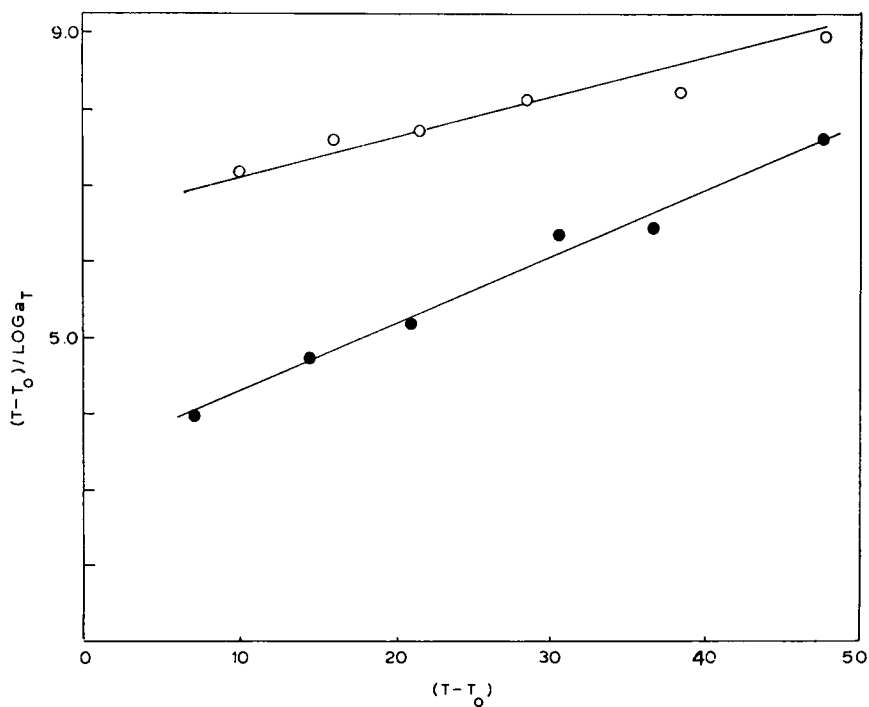


Fig. 9. WLF plots for isotactic and syndiotactic *cis*-1,4-poly-pentadiene vulcanizates: (○) isotactic; (●) syndiotactic.

where B is a constant and is taken as unity. The α_f and f_θ values for the isotactic and syndiotactic forms were calculated to be $\alpha_f = 1.89 \times 10^{-4} \text{ deg}^{-1}$ and $f_\theta = 2.4 \times 10^{-2}$ and $\alpha_f = 9.09 \times 10^{-4} \text{ deg}^{-1}$ and $f_\theta = 2.4 \times 10^{-2}$ respectively. These values are in good agreement with accepted universal values.

SUMMARY AND CONCLUSIONS

Physical characterization of the isotactic and syndiotactic 1,4-poly-pentadiene vulcanizates containing at least 70%–75% *cis* units indicates that the isotactic form is more susceptible to crosslinkage. The ease of vulcanization of the isotactic polymer might be due to its unsaturation being less sterically hindered by methyl groups.

Modulus master curves were determined via the time-temperature superposition principle. The fractional free volume of the vulcanizates at their glass transition temperatures and the thermal expansion coefficients of free volume were in good agreement with accepted values.

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