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Energetic Contribution to the Elastic Force in Polyphenylmethylsiloxane Networks

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ABSTRACT

Energetic contribution to the total elastic force in polyphenylmethylsiloxane networks has been measured in order to elucidate the influence of the phenyl group on chain conformational mobility. A value of 0.20 ± 0.03 for f_e/f was found.

INTRODUCTION

The Gaussian theory for the elasticity of rubberlike materials gives the following expression for the stress [1, 2]:

$$f = nKT \frac{\langle r_i^2 \rangle}{\langle r_0^2 \rangle} (\alpha - \alpha^{-2}) \tag{1}$$

where f is the force on the unit of the cross-sectional area; n is the number of effective elastic chains in the volume unit $\langle r_i^2 \rangle$ and $\langle r_0^2 \rangle$, the end-to-end mean square distances for a network chain and free chain, respectively, and α is the strain ratio defined as L/L_0, L and L_0 being the stretched and unstretched sample lengths.

Assuming that $\langle r_i^2 \rangle \propto V^{2/3}$ at constant volume and length, from Eq. (1) we obtain [3]

$$\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{LV} = -\frac{d \ln \langle r_0^2 \rangle}{dT} \tag{2}$$

According to theory [3], Eq. (2) can be rewritten as

$$\frac{f_e}{fT} = \frac{d \ln \langle r_0^2 \rangle}{dT} \tag{3}$$

where f_e is the energetic contribution to the total stress f and is defined as $(\partial U/\partial L)_{VT}$, U being the internal energy of the system.

In other words, the experimental determination of the ratio f_e/f gives the temperature coefficient of the unperturbed end-to-end distance $\langle r_0^2 \rangle$. It is well known [4, 5] that the term $(d \ln \langle r_0^2 \rangle)/dT$ can give informations about the chain conformation and flexibility.

In the present paper we have analyzed the thermoelastic behavior of polyphenylmethylsiloxane (PPhMS) in order to compare our f_e/f value with the data reported in the literature for the polydimethylsiloxane (PDMS). The purpose is to elucidate the influence of the phenyl group on the chain conformational mobility.

EXPERIMENTAL

The PPhMS samples were supplied by the SNAM Laboratories (Milan). The initiator was dicumylperoxide. The vulcanization was carried out at 160° C for 5 hr. Extraction with benzene in a Soxhlet apparatus for 12 hr did not give evidence of an unvulcanized fraction. Stress-temperature plots were obtained in the usual manner [3], with 1 hr allowed between stress detection at different temperatures.

The temperature range was 30 to 80°C. No hysteresis was observed. The cubic thermal expansion coefficient β was obtained by dilatometric measurements in the temperature range 30 to 90°C. The experimental data give

$$\beta = 8.52 \times 10^{-4}\ \mathrm{deg}^{-1}$$

The molecular weight between two cross-link points, M_c, was obtained by stress isotherms at 50°C carried out on samples swollen with n-hexadecane. The stress f was corrected with the coefficient $V_s^{1/3}$, V_s being the polymer fraction in the swollen network. Data so obtained were treated with the Mooney-Rivlin equation [1] and the results give $2C_1 = 0.91$ kg/cm^2 and $2C_2 = 0.0$ kg/cm^2 in the strain range $\alpha = 1.0$ to 1.5. The zero value for the $2C_2$ term allow us to use the $2C_1$ term to calculate the molecular weight of the network chains [6]. The result was $M_c = 35{,}000$.

RESULTS

From Eqs. (2) and (3) we can write

$$\frac{f_e}{f} = 1 - \frac{T}{f_T}\left(\frac{\partial f}{\partial T}\right)_{VL} \tag{4}$$

When stress-temperature measurements are carried out at constant pressure and length, Eq. (4) must be corrected [3] to

$$\frac{f_e}{f} = 1 - \frac{T}{f_T}\left(\frac{\partial f}{\partial T}\right)_{PL} - \frac{\beta T}{\alpha_T^{\,3} - 1} \tag{5}$$

where f_T and α_T are the stress and the strain at temperature T, respectively.

Typical stress-temperature plots are reported in Fig. 1. Experimental data are collected in Table 1. Different letters refer to different specimens of the same sample.

f_T and α_T are reported in terms of the Mooney-Rivlin equation in Fig. 2 to test the reproducibility of the data and the absence of

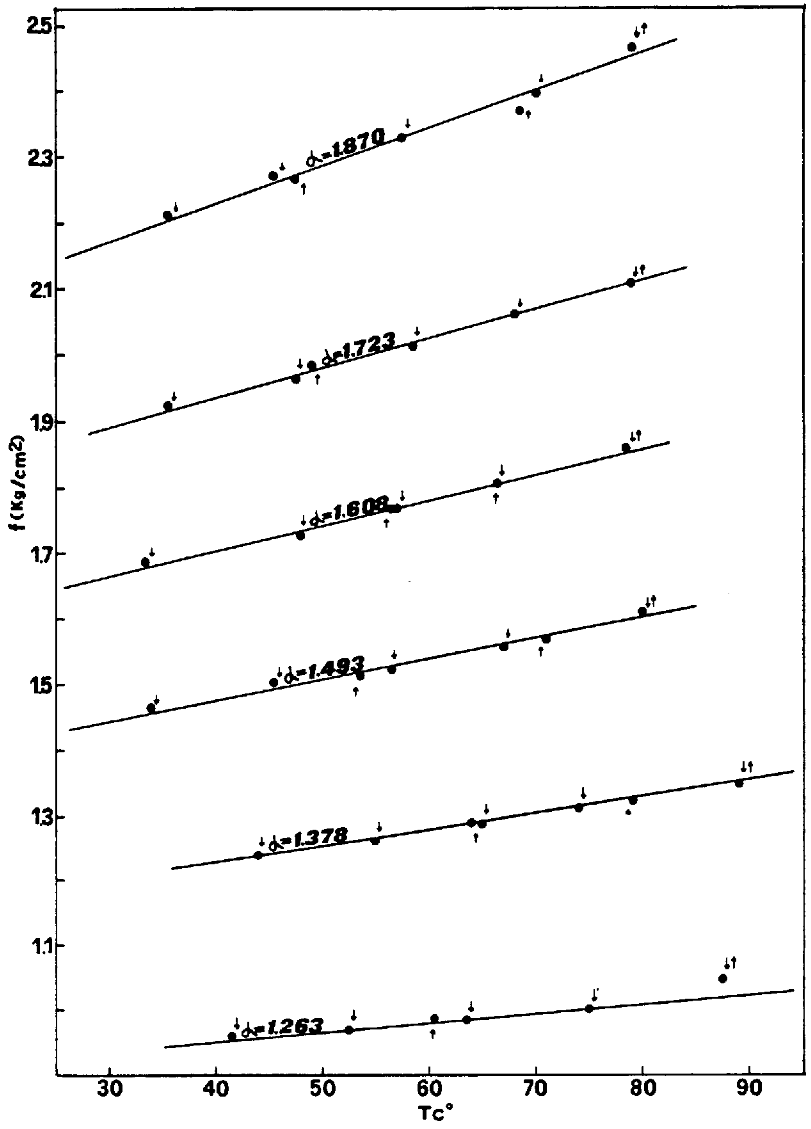

FIG. 1. Stress-temperature plots obtained with Specimen A of Table 1.

TABLE 1

Specimen	α_T	$\bar{f}_{50^\circ}$ (kg/cm^2)	$\partial f/\partial T$ (kg/cm^2 C^{-1})	f_e/f
A	1.870	2.29	5.74×10^{-3}	0.14
	1.723	1.98	4.47×10^{-3}	0.20
	1.608	1.742	3.88×10^{-3}	0.19
	1.493	1.508	3.20×10^{-3}	0.20
	1.378	1.254	2.40×10^{-3}	0.21
	1.263	0.966	1.42×10^{-3}	0.26
B	1.429	1.421	3.02×10^{-3}	0.17
	1.574	1.763	4.27×10^{-3}	0.13
	1.880[a]	2.202	5.30×10^{-3}	0.17
	1.516[a]	1.462	3.00×10^{-3}	0.23
	1.757[a]	2.088	4.83×10^{-3}	0.19
C	1.440	1.544	3.02×10^{-3}	0.23
	1.314	1.260	2.08×10^{-3}	0.25
	1.565	1.805	3.92×10^{-3}	0.20

[a] After extraction with benzene for 12 hr.

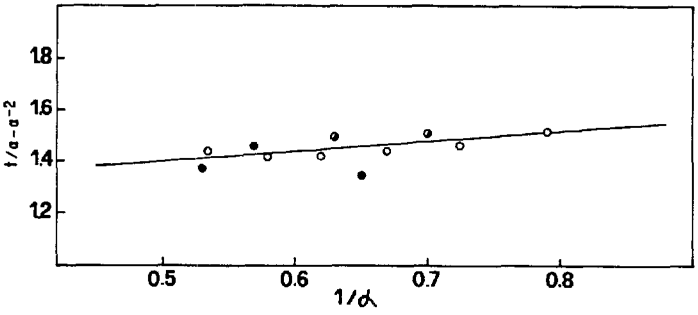

FIG. 2. The f_T and α_T values of Table 1 reported in terms of the Mooney-Rivlin equation. (O) Specimen A. (◐) Specimen B. (●) Specimen B after extraction.

hysteresis phenomena. The data of Table 1 clearly indicate that the f_e/f value is independent on strain, extraction treatment, and specimen used.

The mean value obtained for f_e/f is 0.20 ± 0.03 and, from Eq. (3), this value gives

$$\frac{d \ln \langle r_0^2 \rangle}{dT} = (6.1 \pm 0.9) \times 10^{-4}\ {}^\circ C^{-1}$$

In Table 2a the $(d \ln \langle r_0^2 \rangle)/dT$ value so obtained is compared with the temperature coefficient of PDMS determined from different experimental techniques by different authors [7-11].

TABLE 2a

Polymer	$(d \ln \langle r_0^2 \rangle/dT) \times 10^4$ (°C $^{-1}$)	Method	Ref.
PDMS	8 (70°C)	Thermoelasticity	7
"	5 (80°C)	"	8
"	4 (80°C)	"	9
"	7	Solution data	7
"	3	"	10
"	4	"	11
PPhMS	6.1 (50°C)	Thermoelasticity	This work

It is of theoretical interest to analyze the thermoelasticity results of Table 2a in terms of

$$f_e/f = -\epsilon'/RT \tag{6}$$

where ϵ' has the dimensions of an energy and is correlated to the difference between the trans and gauche energy states in polymeric segments [4]. Data are reported in Table 2b.

DISCUSSION

The purpose of this work was to investigate the role different steric constitutions may have on the flexibility of a macromolecule. In

TABLE 2b

Polymer	$-\epsilon' \times$ °K (cal/mole)	Ref.
PDMS	188.2	7
"	124.6	8
"	99.7	9
PPhMS	127.3	This work

particular, on the basis of data reported in the literature for PDMS, we have analyzed the thermoelastic behavior of a PPhMS network in order to elucidate the relative influence of methyl and phenyl groups on the temperature coefficient of the unperturbed chain dimensions.

The data of Table 2a indicate a tendency of the two polysiloxane to extend on heating.

The good agreement between thermoelastic and solution properties observed for the PDMS, on the other hand, allowed us to analyze our results only in terms of intramolecular interactions without any significative intermolecular component. With this assumption supported by recent results obtained on polyoxyethylene chains [13], we can evaluate the data of Table 2b. As shown, the ϵ' term calculated for the PPhMS chain is intermediate in the values given by different authors for the PDMS chain. On the other hand, we can assume that the presence of a phenyl group should make rotation about the single bond Si—O more hindered, giving a greater value to ϵ'.

Even if this consideration supports the data of Refs. 8 and 9, the effect due to the phenyl group seems to be small and not larger than the experimental error. This result, which is unexpected, can be explained by the following observations. The presence in the PPhMS chain of two different groups on the silicon atom gives two different trans states, owing to the two different absolute configurations of the silicon atom, as shown in Fig. 3.

In Fig. 3a there is a strong Ph—Ph interaction; that is, substituted in Fig. 3b by Ph—Meth interaction. The distribution of the two absolute configurations along the chain is random and the relative presence is 50% and 50%, while the statistical distribution of the different gauche and trans conformational states is ruled by the Boltzmann law. The data of Table 2a indicate that the chain length increases on heating; in other words, on heating there is an increase in the population of the trans states. Of course, the relative statistical weight of the two forms in Figs. 3a and 3b depends on the temperature.

In the temperature range investigated, only the form in Fig. 3b could be statistically important, while the very strong Ph—Ph interaction could be practically absent. Of course, analogous considerations can be made for the gauche and for the intermediate states whose energy depends on the absolute configurations of adjacent silicon atoms. This picture is supported by previous papers [9, 12], where it is clearly demonstrated that the temperature coefficient of the unperturbed chain dimensions is a function of the temperature. In other words, the small difference observed between the PDMS and the PPhMS thermoelastic behavior could be due to the restricted temperature range investigated.

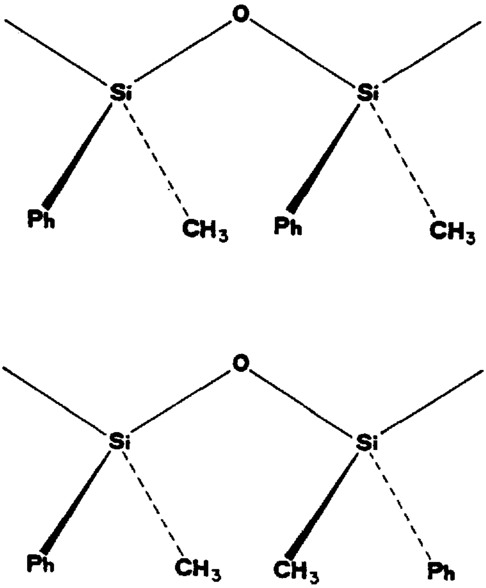

FIG. 3. Two possible trans-planar states which depend on the absolute configurations of the adjacent silicon atoms.

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