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3. Intrachain Interactions in *Cis- Trans-* 1,4-polybutadiene Networks. *Quasi*-isoenergetic macromolecules

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SUMMARY

Thermoelastic data of cis- trans- 1,4- polybutadiene networks swollen in n- octane are presented. On the basis of the theory of the Gaussian chain the analysis of the energy part of the retractive force and of the temperature dependence of the unperturbed dimensions has been carried out as the function of the cis- trans- ratio of the subunits within the macromolecular chains. Temperature invariant macroconformation has been verified by quasi- isoenergetic chains consisting on $\sim$ 40 % trans and 60 % cis- units within statistically arranged cis- trans- polybutadiene networks.

INTRODUCTION

The concept of the Gaussian chain is the fundamental tenet of the kinetic theory of rubber elasticity and is comparable to that of the Maxwell distribution in a gas. A Gaussian chain is defined by the following expression for the number of conformations available to a chain with one end fixed at (0,0,0) and the other free to move within a small volume dx dy dz

$$W(x,y,z)\,dx\,dy\,dz = C \exp[-\beta^2 (x^2+ y^2+ z^2)]\,dx\,dy\,dz \quad , \quad (1)$$

where C is a constant and $\beta = 3/2\langle r^2\rangle_o$. The quantity $\langle r^2\rangle_o$, the mean square end- to- end distance of the free cain, depends on pressure and temperature for a Gaussian chain, but not on elongation.

Assuming a network of Gaussian chains, JAMES [1)] has proved that the number of conformations in a network can be written as a product of the number of conformations of the chains times the number of conformations of the junctions; the number of conformations of the junctions do not depend on the degree of stretching of the chains. From these results the free energy of the network, F_n, may be written

$$F_n = \frac{3}{2}\, kT \,\frac{\langle r^2\rangle_E}{\langle r^2\rangle_o} \quad , \quad (2)$$

where $\langle r^2\rangle_E$ is the end- to- end distance of a chain in the network, and for the free energy of deformation the well- known equation

$$F_{el} = F_n{}^{\lambda} - F_n{}^{o} = \frac{kT}{2}\,\frac{\langle r^2\rangle_E}{\langle r^2\rangle_o}\,(\lambda_x{}^2 + \lambda_y{}^2 + \lambda_z{}^2 - 3) \quad . \quad (3)$$

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In this expression $<r^2>_E$ depends on P and T through the volume

$$\left(\frac{\delta \ln <r^2>_E}{\delta P}\right)_T = \frac{2}{3}\frac{d\ln V}{dP} = -\frac{2}{3B} \qquad (4)$$

$$\left(\frac{\delta \ln <r^2>_E}{\delta T}\right)_P = \frac{2}{3}\frac{d\ln V}{dT} = \frac{2\beta}{3} \quad . \qquad (5)$$

For a Gaussian chain it is essential that $<r^2>_o$ does not depend on elongation, but it may depend on P and T. In general

$$d\ln <r^2>_o = \mu_c dT - V_c dP \quad . \qquad (6)$$

The term $\mu_c = (\delta \ln <r^2>_o / \delta T)_P$ has been recognized by FLORY[2)] to represent the temperature dependence of the statistical length of the molecule in the crosslinked rubber, arising from energetic interactions within the chain. The quantity $V_c = -(\delta \ln <r^2>_o / \delta P)_T$ reflects the difference in effective volume between stretched and unstretched chains, and has been so far neglected.

From the equation for the elastic force

$$f = GA_o(\lambda - \frac{V}{V_o\lambda^2}) \qquad (7)$$

where A_o is the cross- sectional area of the unstretched sample and G the equilibrium shear elastic modulus

$$G = \frac{NkT}{V_o}\frac{<r^2>_E}{<r^2>_o} \qquad (8)$$

SHEN [3)] has arrived at the formula

$$\left(\frac{\delta \ln f}{\delta \ln T}\right)_{V,L} = \frac{d\ln G}{d\ln T} + \frac{\beta T}{3} \qquad (9)$$

by recognizing that the shear elastic modulus is a property of state of the rubber and hence independent of pressure and volume.

By combining this result with the thermodynamic equation of state for elastic systems, the relative energy contribution to rubber elasticity is found

$$\frac{f_e}{f} = 1 - \frac{d\ln G}{d\ln T} - \frac{\beta T}{3} = T\,\frac{d\ln <r^2>_o}{dT} \qquad (10)$$

which provides a basis for the experimental determination of the temperature dependence of the unperturbed macrodimensions.

EXPERIMENTAL VERIFICATION OF THE GAUSSIAN NETWORK

Experimentally for many rubbers the MOONEY- RIVLIN equation has been generally observed

$$f = (C_1 + \frac{C_2}{\lambda})(\lambda - \frac{1}{\lambda^2}) \quad . \qquad (11)$$

Since in this equation the experimental modulus depends on the elongation, such chains are not Gaussian. Several explanations for the non- Gaussian behaviour in bulk polymers have been proposed. Recently FLORY $^{4)}$ has provided a molecular theory to account for the connection between locations of the network junctions and macroscopic strain. Constraints on junctions imposed by surrounding chains are made responsible for the strain dependent departure from idealized "phantom" behaviour. Suffice it here to say that not only such non- Gaussian behaviour disappears at small strains, but such specific influences of neighbours are necessarily dismissed by increased separation between chains (c. f. van der Waals theory of real gases) and hence the need for rubbers swollen in an appropriate solvent at low deformations for the investigation of hindered rotation in macromolecules. The crucial point however is the need of a diluent, which does not affect the rotational potentials of the polymer backbone bonds. Such polymer- diluent pairs have been named equiconformer by the one of us $^{5)}$.

In a foregoing paper (SALVIN and CANTOW $^{6)}$) we have reported thermoelastic measurements on crosslinked 1,4- cis- trans- polybutadienes with the subunits arranged in a statistical manner. These measurements however had been carried out at the bulk network at 60 % elongation. In order to dismiss non- Gaussian effects the measurements discussed in the following are carried out at low deformations in the swollen state.

Materials

Cylindrical samples of crosslinked 1,4- cis- trans- polybutadienes with trans contents between 3 and 83 % were prepared in the following manner as described by SALVIN and CANTOW $^{7)}$: Linear 1,4- cis-polybutadiene (M_w = 240.000, 97 % cis, <1,5 % 1,2) was isomerized in solution - in the presence of a sensitizer - by γ- irradiation. After extraction and drying crosslinking was effected by γ- irradiation of the molded bulk polymer under vacuum.

Force- extension relationships in the swollen state

For the shear elastic modulus measurements cylinders of length to radius ratio equal to 5, with both bases machined on a rotating emery stone, were bonded in the swollen state, with acrylic glue, to metal plates of an INSTRON 1122 stress- strain machine. The apparatus was improved for temperature stability of the air chamber and with special precautions to decouple thermally the measuring strain gauge from the chamber, via Kovar glass tube. The strain gauge was accurately thermostated with circulating liquid and both strain gauge and strain measuring unit were calibrated before and after each experiment. Linearity as well as drift stability of the gauges were found to be excellent.

Deformations up to 30 % maximum (f_{max} = 4,25 N) were applied continuously from compression to extension by manual adjustment of the frame. This was accomplished via a manual screw at the back of the instrument; this could be used instead of the normal servomechanism which caused problems with mechanical vibrations and jumps due to mains- transients. The forces were measured 48 hours after application of sudden compressive stress, and then at intervals of 3 to 5 hours after stepping down the strain, according to temperature. Continuous transition from compression to extension is essential for interpolating to length of sample at zero force, as clearly indicated by WOLF [8] and ERMAN and FLORY [9]. 'Barreling' and'hour- glass' effects due to fixing of the ends set the lower limit of L/R, while buckling which is the most serious source of error sets the upper limit for compression. In connection with buckling (POPOV [10]), EULER' s critical load formula for a column fixed at both ends $f_{cr} = 4\pi^2 EI/L^2$, where E is the modulus of rigidity of the material, I is the moment of inertia and L is the length, is obeyed remarkably accurately in these experiments.

Figure 1 shows the stress- strain isotherms at 283 and 313 K for 1,4- cis- trans- polybutadiene networks, 40 % trans, swollen in n- octane. There are essentially two arguments that n- octane as the swelling agent does not affect the rotational potentials within the polymer backbone. First, high resolution ^{13}C- NMR experiments have shown that n- alkanes of varying chain length have no significant influence on the microconformations. Second, light scattering investigation over a broad temperature range have demonstrated that the FLORY- HUGGINS interaction parameter χ_1 is only slightly dependent on the temperature for the isomer polybutadienes in n- octane - $\sim$ 0,48 - 0,49 -, values approaching the pseudo- ideal value of 0,50 [11].

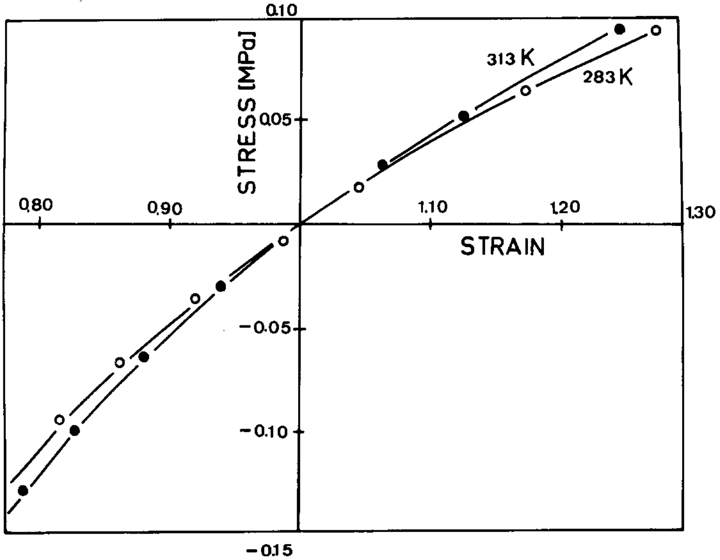

Figure 1: Compression- extension measurements on 1,4- cis- trans- polybutadiene network (40 % trans) at 283 o and 313 ● K

Thermoelasticity and energy part of the retracting force

The equilibrium degree of swelling varies a small amount with temperature and strain. TRELOAR [12] has treated formally a dry rubber as a slightly compressible liquid - i. e. since $(V-V_o)/V_o \sim 10^{-4}$, $\beta \simeq \beta_o$ - and a rubber swollen in equilibrium in a liquid as a highly compressible material. Composition changes have been accounted for by SMITH [13] with the FLORY- REHNER theory of network swelling, for the case where the diluent does not affect the rotational potentials.

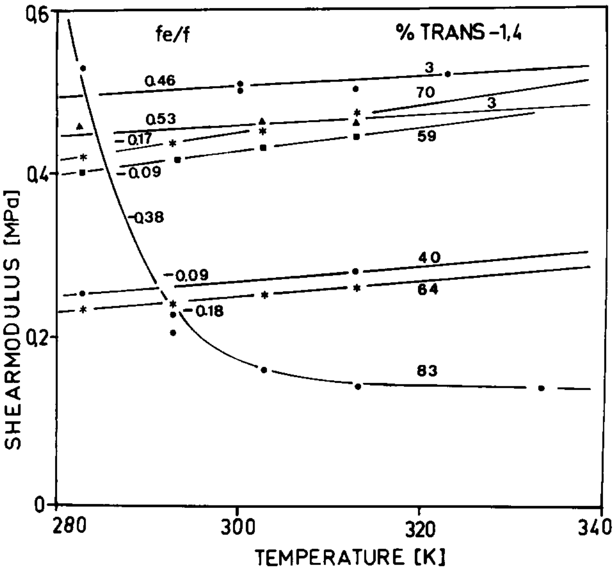

Figure 2: Shear elastic modulus of 1,4- cis- trans- polybutadiene networks swollen in n- octane versus temperature. Trans content and energy part of the retractive force indicated

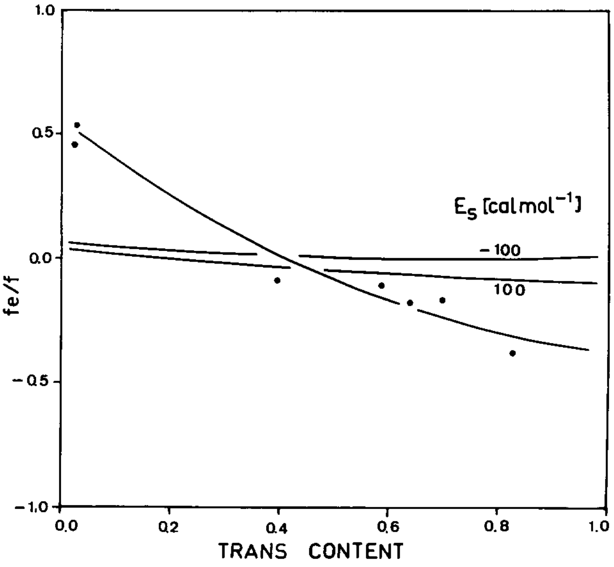

Figure 3: Energy part of the retractive force according to SHEN of 1,4- cis- trans- polybutadiene networks swollen in n- octane. RIS calculations (FLORY- ABE [14]) indicated

In the absence of polymer- diluent interactions, and for highly swollen rubbers at low deformations

$$v = \lambda^{1/2} v_o \quad , \qquad \beta = \frac{5\beta_o}{6} \quad , \qquad (12)$$

where the subscript $_o$ refers to the unstretched sample. Figure 2 presents thermoelastic data in the form of a plot suggested by SHEN' s formula, equation (10), for isomer polybutadiene networks of different cis- trans ratio. The data appear to yield correct values of the temperature coefficient of the unperturbed macrodimensions, except for the 83 % trans material where presumably the strong rise in modulus with decreasing temperature is influenced by the neighboured glass transition of the polymer- diluent pair. It has to be noted also that this polymer shows up slight crystallinity, whereas all other samples are entirely amorphous.

Finally, in Figure 3, the data of f_e/f obtained with SHEN' s formula are compared with theoretical results obtained by FLORY and ABE[14)] by means of rotational isomeric state calculations. For the set of parameters chosen, these calculations appear quite insensitive to polymer microstructure.

It may be noted, that swollen 1,4- cis- trans- polybutadiene networks with ∿ 40 % trans- content behave like built up by quasi- isoenergetic subunits in their mechanical behaviour, due to a intramolecular balance of positive and negative energy contributions by the conformers of the components. Such material exhibits a macroconformation unaltered by temperature. It should be extremely interesting in connection with other equilibrium and dynamical mechanical investigations in bulk and in the swollen state. Note that ^{13}C- NMR investigations of the microconformations indicate that another quasi- isoenergetic macromolecule may be realizable, namely a head- to head polypropylene with a statistical arrangement of meso- and d,l- subunits within the chain [15)].

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