Polymer Bulletin 1, 211–214 (1978)

Polymer Bulletin

Thermoelastic Studies on Polybutadiene Networks

Roger Salvin and Hans-Joachim Cantow

Institut für makromolekulare Chemie der Albert-Ludwigs-Universität,
Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, 7800 Freiburg i. Br.,
Federal Republic of Germany

Summary

An unequivocal correlation between the first coefficient of the MOONEY- RIVLIN equation and the degree of swelling is concluded from stress- strain measurements of cis- trans isomerized polybutadiene networks of varying cis- contents and from corresponding swelling measurements. The second coefficient turns out to be approximately constant, which means that the polymer network is not affected critically by the irradiation although the crosslink density diminishes.
The temperature dependence of the unperturbed dimensions of the network was determined to be positive in the higher cis-region and to be negative at higher trans contents. A linear correlation was found with the amount of trans.

Introduction

In the foregoing paper [1] we described the preparation of cis- trans- polybutadienes by ^{60}Co irradiation of crosslinked cis- polybutadienes in the swollen state with diphenyl disulfide as sensitizer. During irradiation we observed a decrease of the volume fraction of the polymer in the gel ϕ_2.Due to an uncertainity in the values of the FLORY- HUGGINS parameters, χ, for the cis- trans- polymers it could not be concluded unequivocally, however, to which extent the crosslink density was affected.
In the present paper this effect was clarified by stress- strain measurements on the unswollen polymers as well as stress- temperature measurements, the latter having been performed to determine the temperature dependence of the unperturbed dimension of the network.

Experimental

The preparation of the samples varying from 1 to 83 % trans- 1,4 content is described in the foregoing paper [1]. The stress- strain measurements were carried out on strips being 1 mm thick and 10 mm broad with an INSTRON 1122 machine starting at 25° C the force being measured half an hour after elongation. The temperature dependence of the stress was registered at constant elongation - generally $\lambda = 1.60$ - within the range of 25- 95° C. To this purpose the samples were elongated at the maximum temperature and allowed to relax to equilibrium within 45- 150 min according to the sample. With decreasing temperature the corresponding forces reached equilibrium much more rapidly, within 15 min generally. All the experiments were carried out under nitrogen and the exact sample thickness was measured with an inductive transducer gauge.

0170-0839/78/0001/0211/$01.00

Results and Discussion

Typical curves for the reduced force $f^* = f/A(\lambda-\lambda^{-2})$ versus the inverse elongation λ^{-1} are plotted in Figure 1. The curves fit the semi- empirical MOONEY- RIVLIN equation [2] $f^* = 2C_1 + 2C_2\,\lambda^{-1}$. (A = cross section)

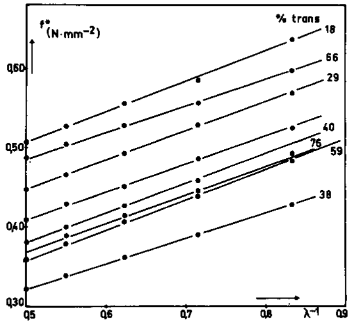

Fig. 1: Typical stress-strain plots for polybutadiene networks at 25° C

Table

% trans	ϕ_2	$2C_1$ $(N \cdot mm^{-2})$	$2C_2$ $(N \cdot mm^{-2})$	χ	f_e/f
< 1	0.113	0.138	0.287	0.35	
< 1	0.157	0.210	0.359	0.39	0.18
< 1	0.183	0.278	0.412	0.42	0.16
< 1	0.221	0.366	0.390	0.42	0.16
18	0.205	0.331	0.352	0.42	0.18
22	0.208	0.300	0.380	0.37	
23	0.155	0.195	0.364	0.40	0.043
29	0.180	0.257	0.380	0.41	0.076
30	0.196	0.274	0.340	0.38	
36	0.185	0.256	0.373	0.38	0.059
38	0.132	0.166	0.312	0.37	0.13
38	0.135	0.153	0.394	0.39	0.014
40	0.144	0.196	0.368	0.37	0.031
42	0.163	0.173	0.326	0.43	0.018
52	0.127				- 0.017
52	0.168	0.234	0.348	0.40	0.007
53	0.111	0.142	0.385	0.39	- 0.021
53	0.134	0.160	0.356	0.38	- 0.033
53	0.135	0.182	0.368	0.39	- 0.033
61	0.142	0.175	0.332	0.38	- 0.020
65	0.136	0.170	0.348	0.37	- 0.13
66	0.172	0.284	0.374	0.37	- 0.093
76	0.115	0.165	0.384	0.31	- 0.10
83	0.110	0.150	0.325	0.37	- 0.12

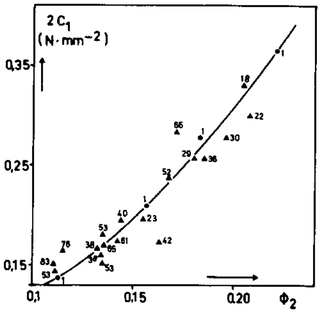

Fig. 2: 2 C_1 versus ϕ_2 for the networks swollen in toluene. % trans indic.

The values of 2 C_1 and 2 C_2 are tabulated in the Table. In Figure 2 the first coefficient is plotted versus the volume fraction of the polymer in the sample swollen in toluene, ϕ_2, as determined before for each sample.

First, all samples - unisomerized cis- polybutadienes included - irrespective of the configuration fit one curve within experimental error. Secondly the 2 C_2 parameter is practically constant, 0.359 av. Consequently crosslinking is decreasing with ϕ_2 assuming that C_1 is proportional to ν, the number of network chains per unit volume. So it is affirmed that the diminution of ϕ_2 with the irradiation time as found is caused by a corresponding drop in the crosslink density.

On the basis of our results it is possible now to check the assumption made in the previous paper, namely that the interaction parameter χ is not critically dependent on the cis- trans arrangement in the polymer. Column 5 of the table presents the values obtained for χ assuming that $2\,C_1 = \nu kT$ [3] and that ν is correlated to χ by the FLORY- REHNER equation [4] :

$$\nu = - \frac{1}{V_s} \cdot \frac{\ln(1-\phi_2) + \phi_2 + \chi \phi_2^2}{[\phi_2^{1/3} - \frac{\phi_2}{2}]} \qquad (1)$$

V_S = molar volume of the solvent

The average value found for $\chi = 0.385$ agrees well with the value determined for cis- polybutadiene in toluene at 25° C, which would support our assumption. Analyzing the data of the table by regression analysis it turns out however that the χ- value has a certain variance within the measured range between 0.40 (for high cis) and 0.36 (for high trans). This tendency could be assured by recent light scattering experiments on high cis- polybutadienes too [5]. These minor deviations do not influence however our conclusions.

From the approximate constancy of the 2 C_2 parameter it may be concluded that the polymer network is not critically affected by the radiation induced chain scission because constant C_2 means constant deviation from gaussian chain statistics [4]. On the other hand the fact that the 2 C_2 parameters fit the same curve as the initial cis- polybutadiene is an additional argument.

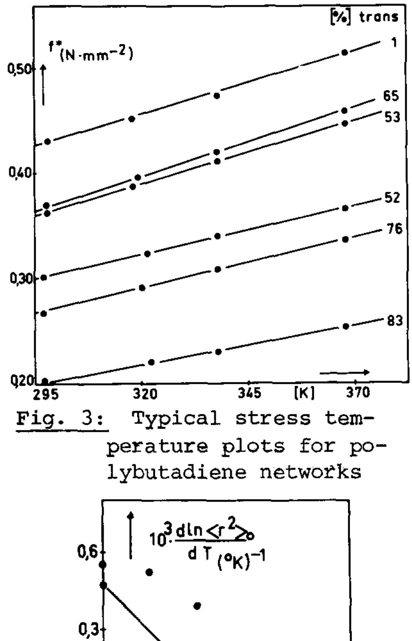

Fig. 3: Typical stress temperature plots for polybutadiene networks

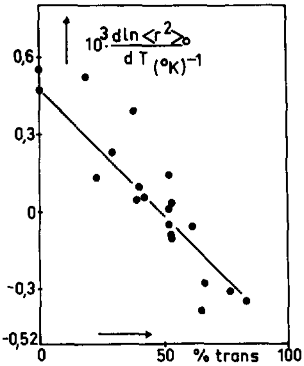

Fig. 4: T- dependence of the unperturbed dimensions versus % trans

Typical plots of the reduced force versus temperature at constant elongation are presented in Figure 3. Evaluations have been made on the basis of FLORY' s equations [6]:

$$\frac{f_e}{f} = T\, d\ln\langle r^2\rangle_o / dT = \qquad (2)$$

$$- T[\delta \ln(f^*/T) / \delta T]_{p,L} - \beta T/(\alpha^3 - 1)$$

f_e = energy part of the retracting force f

$\langle r^2 \rangle_o$ = unperturbed chain dimension

β = thermal expansion coefficient, which is assumed to be constant and equal to $6.9 \cdot 10^{-4}\ K^{-1}$

α = relative extension at constant volume

With

$$T[\delta \ln(f^*/T) / \delta T]_{p,L} = [\frac{\delta \ln(f^*/T)}{\delta \ln T}]_{p,L} = \langle \frac{T}{f^*} \rangle (\frac{\delta f^*}{\delta T})_{p,L} - 1$$

$(\frac{\delta f^*}{\delta T})_{p,L}$ is given by the slopes of f^* versus T and $\langle T/f^* \rangle$ is averaged from all experiments. The f_e/f values are presented in the last column of the table. Figure 4 finally shows the temperature coefficient of the unperturbed dimensions versus the trans content of the samples. It turns out that the temperature coefficient is positive down to ~50 % trans and turning to be negative at higher trans contents. Furthermore the correlation is a linear one within experimental accuracy. Good agreement was found with the values given in the literature for high cis- and for high trans- polybutadiene [7]. It may be stated that the inversion of the temperature coefficient of the unperturbed dimensions with the primary structure of the macromolecules means a corresponding change in the populations of the conformations of the structural units. Up to now this effect could not be explained quantitatively with the aid of semiempirical force field calculations. J. E. MARK [7, 8] however has discussed the origin of the different sign of the temperature coefficients of the unperturbed dimensions of 1,4- cis- and 1,4- trans- polybutadienes in terms of different compactness of the respective chain conformations.

We have to thank DEUTSCHE FORSCHUNGSGEMEINSCHAFT for financial support and the ALEXANDER VON HUMBOLDT- STIFTUNG for personal financiation (R.S.)

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Received October 6, 1978