Polymer Bulletin 1, 161–165 (1978)

Polymer Bulletin

Radiation Induced Cis-Trans Isomerization of Swollen Polybutadiene Networks

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Summary: The kinetics of the radiation induced cis- trans- isomerization of cis- 1,4- polybutadiene gel swollen in toluene were studied by using diphenyl disulfide as sensitizer. The reaction follows first order kinetics. The values of the pseudo first- order rate constant of the isomerization vary with the crosslink density of the network. After correction for the degree of swelling, however, the isomerization reaction turns out to be independent of the crosslink density and proceeds with the same efficiency as in solution.

Introduction

The radiation induced cis- trans isomerization of polybutadienes has been studied intensively. For the case of diphenyl sulfide as the sensitizer GOLUB [1] particularly proposed a mechanism involving complexing and dissociation of mercaptyl radicals with subsequent formation of the thermodynamically favoured trans isomer.

Since the study of the mechanical properties of polybutadienes requires crosslinked materials, isomerization of crosslinked samples seemed to be an approach to synthesize test specimens of varying cis-trans content. The present paper is concerned with the kinetics of the cis- trans isomerization of swollen cis-1,4- polybutadiene gels under ^{60}Co γ- radiation with diphenyl disulfide as sensitizer. The behaviour of the network during irradiation was studied, too.

Experimental

The polymer used in this study was a practically linear polybutadiene with 98 % cis- content (<1 % trans, >1 % 1,2) provided by Chemische Werke Hüls, with an osmotic M_n of 256 000. For the network preparation aluminum square moulds containing the polymer were pressed at 100° C under 50 torr for one hour. After cooling the moulds were exposed to the ^{60}Co γ- radiation at 6 to 25 Mrad. The uncrosslinked material was extracted with toluene during one month. Then the solvent was evaporated in vacuo.

The crosslink density ν has been determined by swelling using the FLORY-REHNER equation [2]

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

where ϕ_r is the volume fraction of rubber in the swollen gel, V_s the molar volume of the solvent and χ the FLORY- HUGGINS interaction parameter. Data from literature and our own preliminary light scattering data did

0170-0839/78/0001/0161/$01.00

not exhibit a significant shift in χ neither due to the cis- trans [3] ratio nor due to ν in the investigated range[4]. Thus, in a first approximation χ was taken constant and equal to 0.39. Figure 1 shows the variation of ϕ_r and ν with the radiation intensity.

To acheive isomerization the crosslinked samples were swollen for three days in a toluene solution of diphenyl disulfide in amber- coloured bottles under nitrogen. Then the bottles are exposed to the ^{60}Co source for different periods of time. After irradiation the sulfur residues were extracted during one month. The sulfur remaining was <0.5 % as determined by microanalysis.

The degree of isomerization was determined by ^{13}C NMR in the networks swollen in $CDCl_3$ [5]. The solvents used for the extraction and for the irradiation experiments contained 0.1 % α- naphthylamine as antioxidant.

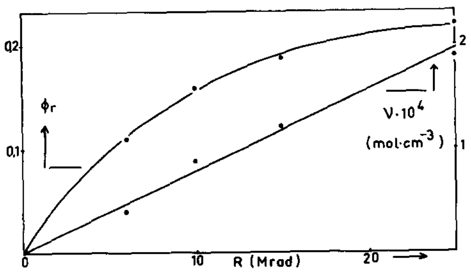


Fig. 1: ϕ_r and ν vs. dose absorbed

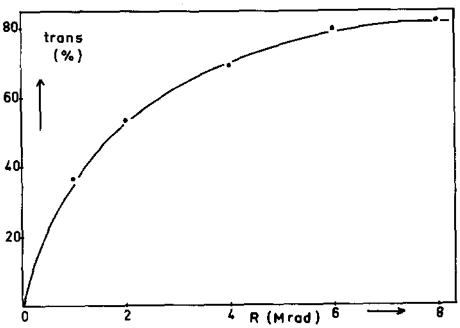


Fig 2: Isomerization of a swollen gel (ν= 0.88· 10^{-4}, [ΦSSΦ]= 1.22· 10^{-4} mol·cm^{-3}) versus dose absorbed

Results and discussion

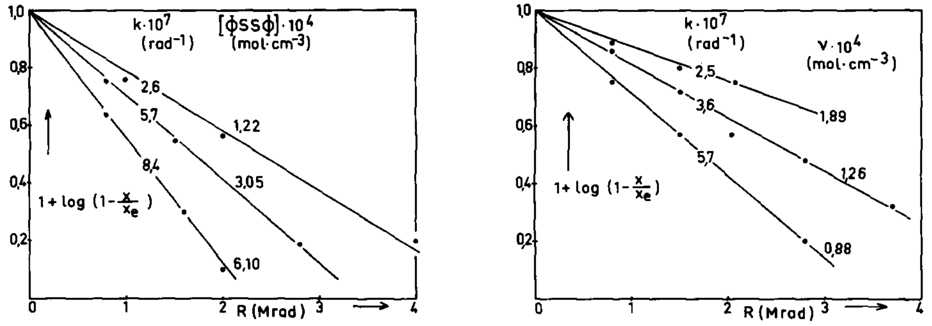
The isomerization of a swollen cis- 1,4- polybutadiene gel as a function of the radiation dose absorbed is demonstrated in figure 2. The equilibrium is reached at ∿83 % trans, and this corresponds well with the figure of 80 % as determined by GOLUB [1] for the isomerization of linear polybutadienes in solution.

The pseudo first- order rate constant k for the isomerization is given by the following expression for a reversible first order process, i. e. the addition of the mercaptyl radical on the double bond,

$$k = - \frac{2.303\ K}{1 + K} \cdot \frac{d \log(1 - \frac{x}{x_e})}{dR} \qquad (2)$$

where K is the equilibrium constant for the isomerization and x and x_e is the amount of cis converted to trans at a radiation dose R and at equilibrium, respectively. With x_e = 83 % K is equal to 4.9 for the isomerization at room temperature.

Figure 3 presents the kinetic plots for various sensitizer concentrations. According to figure 4 k seems to be a function of the crosslink density. The higher value of k apparently indicates a more rapid isomerization of



Figures 3 and 4: Kinetic plots for the isomerization of swollen gels
with $\nu = 0.88 \cdot 10^{-3}$ mol· cm^{-3} at various ΦSSΦ concentrations — with different crosslink densities ν at [ΦSSΦ] $= 3.05 \cdot 10^{-4}$ mol· cm^{-3}

lower crosslinked samples. The variation of the rate constant with ν dissappears however if one assumes, that only the sensitizer molecules inside the swollen gel are responsable for the isomerization.

The number of cis- double bonds isomerized per 100 e.v. of energy absorbed in the swollen gel, G, which is a kind of quantum yield, may be calculated now, if we make the additional assumption, that the sensitizer absorbs the entire radiation; there is no energy transfer from solvent molecules to the solute or vice versa. The absorbance of the sensitizer is taken to be $5.6 \cdot 10^{19}$ e. v. per g of sensitizer per Mrad.

Table: Radiation induced isomerization of swollen cis-1,4- polybutadiene gels

[ΦSSΦ]·10^4 (mol·cm^{-3})	$\nu \cdot 10^4$ (mol·cm^{-3})	k·10^7 (rad^{-1})	$G_o \cdot 10^{-4}$
6.10	0.88	8.4	0.7
	1.26	4.2	
	1.89	2.8	
3.05	0.88	5.7	1.4
	1.26	3.6	
	1.89	2.5	
1.22	0.88	3.9	6.8
	1.26	2.6	
	1.89	1.7	
0.96 [1]	0	59.6	6.0

Since G is changing drastically with the dose we define, according to GOLUB [1], G_o, which is determined by extrapolating G to zero dose. The table demonstrates that G_o decreases strongly with the disulfide concentration. GOLUB [1] has interpreted this correlation in solution by an increased combination rate of mercaptyl radicals at higher [ΦSSΦ], which would reduce the chain length of the reaction and thus the calculated energy yield for the thyil radicals.

One notes that the isomerization rate constant is drastically higher in solution as even in weak gels, due to hindered mobility of the sensitizer in the network. So it becomes plausible that only the amount of sensitizer within the gel is relevant for the isomerization reaction. The fair agreement between the G_o values for both reactions - linear polymer in solution and swollen

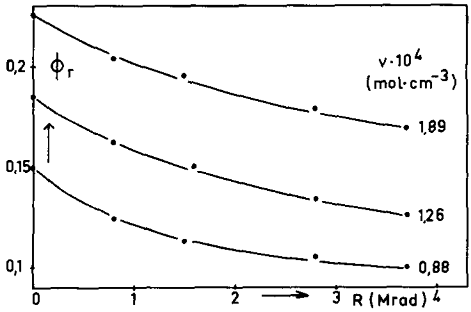


Fig. 5: ϕ_r versus dose absorbed at $[\Phi SS\Phi] = 3.05\cdot 10^{-4}$ mol· cm^{-3}

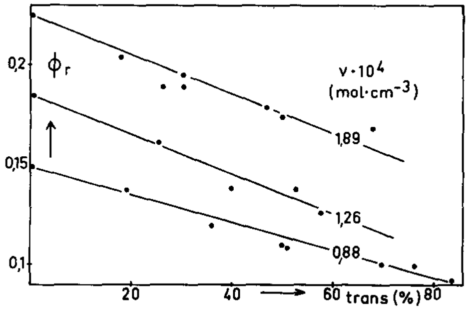


Fig. 6: ϕ_r versus trans content with ν as parameter

gel, respectively - at comparable sensitizer concentrations proves, that the reactions occur with the same mechanism and with the same efficiency.

During the isomerization process a certain decrease of the volume fraction of the polymer in the swollen gel has been observed, as demonstrated in figure 5 at $[\Phi SS\Phi] = 3.05\cdot 10^{-4}$ mol· cm^{-3} for the different ν. Figure 6 shows that, within experimental error, for constant crosslink density all runs carried out with differing sensitizer concentrations are located on the same curve, if one plots ϕ_r versus trans content.

Even if one assumes that the interaction parameter χ is not strictly independent on the cis- trans ratio within the macromolecule, a limited diminuation of the crosslink density must be concluded. χ could decrease only moderately with increasing trans. Similar effects are described in the literature for solution studies by BERGER and BUCKLEY [6], GOLUB [7] and SEELY [8]. Increase as well as decrease of the STAUDINGER index were observed during irradiation. Residual oxygen is discussed as the reason for such effects. Viscosity measurements alone are not conclusive however. An influence of traces of oxygen is plausible in our experiments. With a $[\Phi SS\Phi] = 1.22\cdot 10^{-4}$ mol· cm^{-3} and 1.5 Mrad we found 30.1 % trans and $\phi_r = 0.192$ under nitrogen and 22.2 % trans and $\phi_r = 0.175$ under air. If χ would decrease with increasing trans also ϕ_r would decrease a little bit. The significant inverse effect found demonstrates the chain scission due to oxygen.

Mechanical measurements of isomerized samples are in progress with the aim to clarify unequivocally the influence of oxygen on the crosslink density as well as the influence of the cis- trans enchainment on the stress- strain behaviour and consequently the segmental conformations.

We have to thank the Deutsche Forschungsgemeinschaft for financial support, the Alexander von Humboldt- Stiftung for personal financiation (R. S.) and the Chemische Werke Hüls AG, Marl for the polybutadiene.

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Received August 2, 1978