Polymer Bulletin 4, 563–568 (1981)

Polymer Bulletin

Sol Fraction and Swelling Analysis of Cis-1,4-Polybutadiene Networks Produced by High-energy Irradiation

G.A. Alvarez, H.-J. Cantow, A. Hasenhindl

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Straße 31,
7800 Freiburg i.Br., Federal Republic of Germany

Herrn Professor Dr. K. Überreiter zu seinem 70. Geburtstag gewidmet

SUMMARY

Soluble fraction and equilibrium swelling in toluene were investigated on cis-1,4-polybutadiene networks being crosslinked in vacuo by ^{60}Co-irradiation. Analysis of the sol fraction data by means of INOKUTI's equation reveals a drastic increase of the degradation-crosslink ratio for samples unpurified prior to crosslinking. Furthermore, the network crosslinking susceptibility depends on purification , although it is rather temperature insensitive for irradiation above the glass transition temperature of the rubber. The statistics of creation of crosslinks can be examined by suitable modification of INOKUTI's theory. From the present data it may be concluded that chain reaction crosslinking is negligible. The FLORY-REHNER formula for swelling equilibrium fails to reproduce the data at the crosslink densities studied, but introducing a free end correction, the formula becomes applicable, with some over-correction. Hence the crosslink susceptibility could be obtained independently if the polymer-solvent heat interaction parameter were known. Additionally, the assumption about the proportionality of the crosslink density with radiation dose has been successfully tested by the swelling experiments.

INTRODUCTION

Network formation by high energy radiation offers considerable advantages over chemical methods mainly because accurate doses can be applied and very pure networks of a random type may be produced. One main drawback of radiation methods in bulk polymers is degradation of the chains caused by the presence of oxygen as well as of impurities. A ratio of crosslink to degradation density characterizes the network formed. Additionally, network formation by chain reaction, i. e. where a single ionization or excitation event gives rise to more than one link, is possible. The occurence of an initial non- random molecular weight distribution complicates the analysis. The present study is motivated by the need to characterize networks prepared for thermoelastic measurements.

SAITO (1958) has introduced a basic equation for the changes in molecular weight distribution due to crosslinking of linear polymers of initially arbitrary molecular weight distribution, based on the following assumptions: 1) random crosslinking, 2) probability of crosslinking is independent of position or type of structural unit, 3) the number of crosslinks is small compared to the number of structural units, and 4) there is no short-range intramolecular crosslinking. The modified SAITO equation for post-gel irradiation is

$$\frac{1}{p}\frac{\partial w(p,x)}{\partial x} = -2w(p,x) + \int_{0}^{p} w(l,x)w(p-l,x)\,dl \quad . \qquad (1)$$

0170-0839/81/0004/0563/$01.20

With $w(p,x)$ the weight fraction of molecules contained in the sol and having p structural units, this equation expresses the change in $w(p,x)$ with respect to the density of crosslinks . The left hand side is the rate of increase of the number of molecules of p structural units, the second term in the right side gives the rate with which the molecules of p structural units are produced by crosslinking the molecules of 1 units with those of p- 1 units. This equation is to be solved with a given initial value of $w(p,0)$.

When a polymer substance, whose molecular size distribution is given by a weight fraction function $w(p)$, undergoes crosslinking whose density is x and main chain scissions of density y, it is necessary first to calculate, by means of the analogue of Equation 1 for scission, the modified weight fraction $w(p,y)$ due to scission, and then, considering the crosslinking effect, to obtain the weight fraction $w(p,x,y)$ by solving Equation 1 under the initial condition $w(p,0,y) = w(p,y)$. The integration of Equation 1 proceeds normally by means of LAPLACE transform techniques.

The relationship between gel fraction and the density of crosslinks x and main chain scissions y is generally given, for an initial SCHULZ-ZIMM distribution, as follows (INOKUTI, 1963)

$$1 - g = \frac{1}{(xg+y)^3}\left\{\frac{2xyg}{u} + y^2(xg+y) - \frac{2yg}{u}\left[1 + \frac{u(xg+y)}{\sigma}\right]^{-\sigma} + x^2g^2(xg+y)\left[1 + \frac{u(xg+y)}{\sigma}\right]^{-\sigma-1}\right\} \qquad (2)$$

where u is the number average degree of polymerization and σ is a parameter indicating the narrowness of the distribution breadth. The weight average degree of polymerization of the SCHULZ-ZIMM distribution is equal to $u(\sigma+1)/\sigma$.

For an initial random distribution, $\sigma=1$, and Equation 2 becomes

$$s + s^{1/2} = \frac{y}{x} + \frac{1}{xu} \qquad (3)$$

which is the CHARLESBY-PINNER relationship, where s is the sol fraction and $s = 1- g$ (CHARLESBY and PINNER, 1959). Since the density of crosslinks x and that of the main chain scissions y are usually proportional to radiation dose, i. e. $x = x_0r$ and $y = y_0r$, the plot of $s+s^{1/2}$ versus reciprocal radiation dose gives a straight line.

When the initial molecular size is not the random distribution, the plot of $s+s^{1/2}$ versus reciprocal radiation dose is not linear. In this case the CHARLESBY-PINNER plot is convex upward for $\sigma>1$ and concave upward for $\sigma<1$. Deviations from straight line behaviour even for $\sigma=1$, may indicate disagreement with an initial SCHULZ-ZIMM distribution.

EXPERIMENTAL

97 % cis- 1,4- polybutadiene (< 1 % 1,2 units, CHEMISCHE WERKE HÜLS AG) has been characterized by osmometry, light scattering and gel permeation chromatography (ANDRESS, 1980)

M_n (osm)	M_w (LS)	M_n (GPC)	M_w (GPC)	M_z (GPC)	M_{z+1} (GPC)
218.000	488.000	216.000	498.000	1.078.000	1.942.000

Two sets of samples were prepared for irradiation, one set was purified and carefully outgassed by dissolving in toluene and precipitating from methanol, the other set were samples as delivered from the manufacturers, which contained a small amount of antioxidant. Strips of 30·2·2 mm were moulded under pressure, weighed, evacuated to 10^{-4} torr and sealed in glass ampules, and irradiated in a ^{60}Coγ-ray cell at 5 kGy/hr. Again, one set of samples was irradiated at the cell temperature of 35°C, and another at -70°C in a Dewar vessel containing solid CO_2. No weight loss or bubbles could be detected after irradiation. The irradiated strips were swollen in toluene for eight to ten weeks in presence of 0,1 % antioxidant and then weighed. Samples swollen for eight weeks were indistinguishable from those swollen for ten weeks. The location of the point where the strips held their shape was estimated between five and ten kGy. The strips were then dried and weighed again. No carbon-oxygen or double bonds could be detected from NMR spectra of swollen gels.

RESULTS AND DISCUSSION

Figure 1 presents soluble fraction results in a conventional CHARLESBY-PINNER plot. For a random distrubution a straight line should be expected where the intercept gives the degradation to crosslink ratio, and from the slope, the crosslink susceptibility may be obtained. y/x =0,085, 0,0726 and 0,0121 were found. The gel point - s=1 - is also obtainable from this plot .

However, CHARLESBY-PINNER plots are non-linear for non-random distributions. Ignoring at present the small deviation from randomness - σ=0,8 in our case -, a temperature effect of 3 % in the crosslinking rate can be observed, with a reasonable variance, between -70 and +35°C, and a larger increase of 10 % due to removing the antioxidant and outgassing the original samples. A negligible reduction in degradation is achieved by lowering the temperature of the sample during irradiation and dramatic reduction is achieved by purification and outgassing of the rubber. Furthermore, both factors of degradation and crosslink reactivity appear to be coupled, as if the factors influencing degradation were to deactivate somehow the crosslinking reaction.

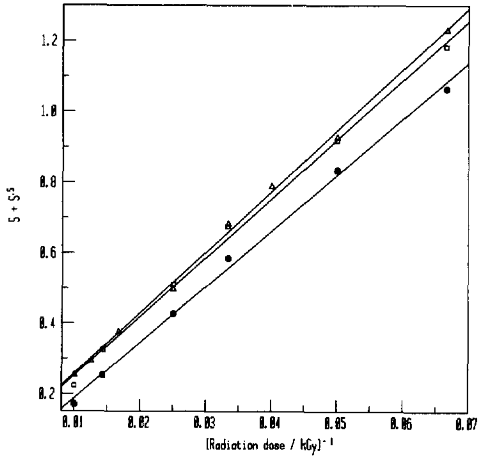

Figure 1: CHARLESBY-PINNER plot of 97 % cis-1,4-polybutadiene, Δ original sample at 35°C and ☐ -70°C, ● sample purified prior to crosslinking

Changes in molecular weight distribution due to irradiation of polymer samples of arbitrary initial molecular heterogeneity appear to be well understood by means of SAITO's theory and its modification by INOKUTI.

A preliminary explanation of the parameters of INOKUTI's equation has been attempted. Figure 2 shows the effect of the degradation-crosslink ratio on the sol fraction; at higher degradation density the sol fraction tends to a plateau with increasing radiation dose. In Figure 3 the curves become displaced along the abscissa with increasing crosslink susceptibility, indicating that for samples with differing susceptibilities the radiation exposure times must be adjusted proportionally in order to achieve constant crosslink density. Figure 4 presents the effect of changing the breadth distribution parameter of the SCHULZ-ZIMM distribution; the effect is necessarily small for small changes in the parameter.

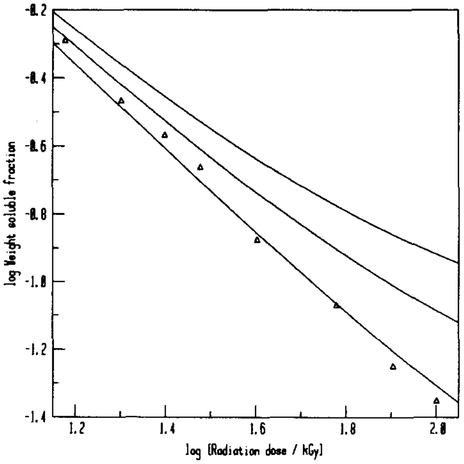

Figure 2: log weight soluble fraction versus log radiation dose for 97 % cis-1,4-polybutadiene. From top to bottom: y/x = 0,3, 0,2 and 0,1. Original sample, irradiated at 35°C

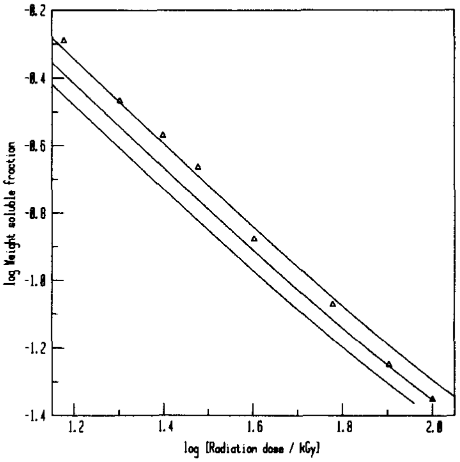

Figure 3: log weight soluble fraction versus log radiation dose for 97 % cis-1,4-polybutadiene. From top to bottom: crosslink susceptibility 1,4, 1,6, 1,8·10^{-5}. Orig. sample irrad.35°C

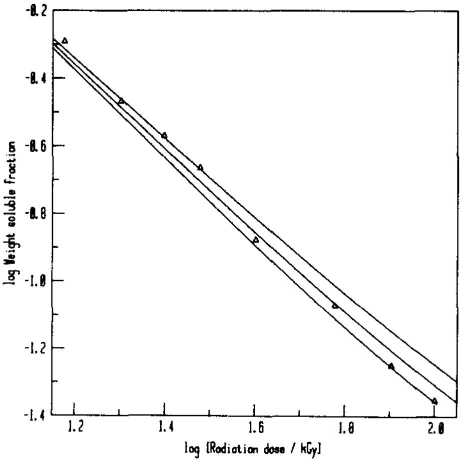

Figure 4: log weight soluble fraction versus log radiation dose for 97 % cis-1,4-polybutadiene. From top to bottom: σ = 0,6, 0,8 and 1,0. Original sample, irradiated at 35°C

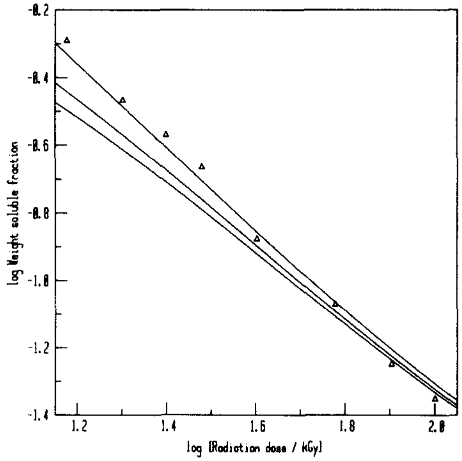

Figure 5: log weight soluble fraction versus log radiation dose for 97 % cis-1,4-polybutadiene. Chain reaction crosslinking parameter 1,0, 0,8, 0,6. Original sample, irradiated at 35°C

The possibility of chain reaction crosslinking, where one excitation event gives rise to more than one crosslink, is taken into account in Figure 5, by means of a statistical analysis due to SCOTT (1964) where

$$g = 1 - \sum_{x=1}^{\infty} w_x s^{x-1} \qquad (4)$$

and w_x is the fraction of crosslinked units of x consecutive units.

$$w_x = \frac{x(x-1)i^3(1-i)^{x-2}}{2} \qquad (5)$$

1/i is the kinetic chain length; for random tetrafunctional networks, i=1 and Equation 5 becomes g=1-s. There is no evidence for i≠1 from our results.

Swelling at low degrees of crosslinking

According to the classical theory (FLORY, 1953) the free energy change ΔF when solvent and network are brought together may be written $\Delta F = \Delta F_M + \Delta F_{el}$ where ΔF_M , the FLORY-HUGGINS free energy of mixing is

$$\Delta F_M = kT(n_1 \ln v_1 + \chi_1 n_1 v_2) \qquad (6)$$

where n_2 has been made equal to 0 since the number of individual polymer molecules in the network is zero. n_1 is the number of solvent molecules and v_1 their volume fraction, χ_1 is the heat interaction parameter.

ΔF_{el} is given by the affine elasticity theory, for isotropic swelling of tetrafunctional networks ($\alpha_x=\alpha_y=\alpha_z$)

$$\Delta F_{el} = \frac{kT\nu_e}{2}(3\alpha_s^2 - 3 - \ln\alpha_s^3) \qquad (7)$$

where ν_e is the effective number of chains in the network. The term $\ln\alpha_s^3$ in FLORY's theory accounts for the entropy of distribution of the $\nu_e/2$ crosslinks over the volume $V_o\alpha_s^3=V$.

At equilibrium the chemical potential difference is required to be zero and thereby the FLORY-REHNER equation is obtained

$$\ln(1-v_2) + v_2 + \chi_1 v_2^2 + \frac{\mu\nu_e}{V_o}(v_2^{1/3} - \frac{v_2}{2}) = 0 \quad . \qquad (8)$$

μ is the molar volume of the solvent.

The FLORY- REHNER equation has been plotted versus two sets of experiments in Figure 6, where, assuming additivity of polymer-solvent volume

$$\frac{1}{v_2} = 1 + \frac{\bar{x}_1 w_1}{\bar{x}_2 w_2} \qquad (9)$$

ω_2 is the weight fraction of the polymer and $\bar{x}_2$ its specific volume. The parallel displacement of the two curves is due to the variation in crosslink susceptibility for the two samples being irradiated at +35 and -70°C, resp. The original FLORY-REHNER formula would show almost no upward curvature in this diagram and would converge with drawn line at high crosslink density. Semiquantitative agreement with the experiment is made possible by applying FLORY's correction for non-elastically-active ends

$$\frac{1}{M_c} = \frac{1}{M_c'} - \frac{2}{M} \quad . \qquad (10)$$

Some degree of over-correction is observed even for $M=1{,}5M_n$. Better end corrections would be necessary to fit this region.

Finally, Figure 7 presents results of an independent test made by solving for M_c in Equation 8 by means of swelling measurements. The strict proportionality expected between M_c and radiation dose is only applicable at very low M_c.

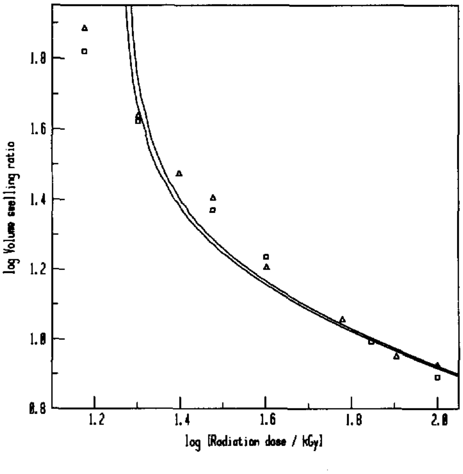

Figure 6: log volume swelling ratio versus log radiation dose. Original sample Δ +35°C and ◻ -70°C

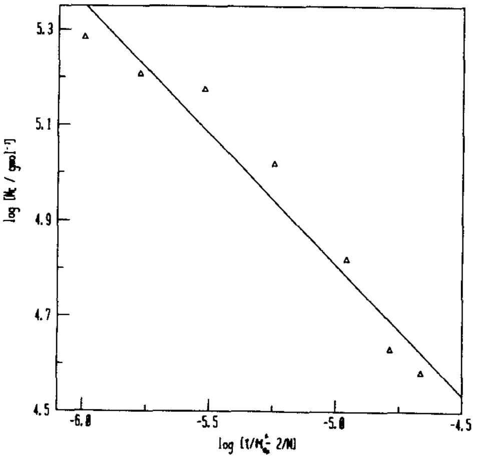

Figure 7: log M_C versus log$[1/M_C' - 2/M]$ for original 97 % cis-1,4-polybutadiene sample irradiated at +35°C

A log-log plot of Equation 10 should yield a straight line of slope equal to -1. Complications arise from the free ends, nevertheless the experimental slopes of -0,6 may be considered to contribute as experimental proof of the validity of the proportionality between M_C and radiation dose.

Crosslinking and simultaneous or consecutive degradation of macromolecules are widely encountered, e. g. free radical, thermal, photochemical and mechanochemical degradation and crosslinking. Therefore recent theoretical approaches in this context are of great interest.

DUSEK (1980) has modified GORDON's cascade theory to account for degradation of primary chains and also for crosslinking by end-linking and crosslinking due to degradation. He also points out sources of error and compares INOKUTI's theory with more accurate theory of branching processes.

It is of great interest to extend these calculations to copolymers of random size distribution, for example cis-trans-polybutadienes, where at least two types of structural units are present.

Financial support by DEUTSCHE FORSCHUNGSGEMEINSCHAFT and by MINISTERIUM FÜR FORSCHUNG UND TECHNOLOGIE is gratefully acknowledged. Dr. GOLDBACH from CHEMISCHE WERKE HÜLS AG we have to thank for the cis-1,4-polybutadiene.

REFERENCES

1. O. SAITO, J. Phys. Soc. Japan 13, 198, 1451, 1465 (1958)
2. M. INOKUTI, J. Chem. Phys. 38, 2999 (1963)
3. A. CHARLESBY and S. H. PINNER, Proc. Roy. Soc. [London] A249, 367 (1959)
4. P. J. FLORY, Principles of Polymer Chemistry, Ithaca, Cornell Univ. Press [1953]
5. H. ANDRESS, private communication
6. K. W. SCOTT, Polymer Preprints 5, 757 (1964)
7. M. DEMJANENKO and K. DUSEK, Macromolecules 13, 571 (1980)

Received April 21, 1981

Responsible for the text: The Editors (see inside title page of this issue). For advertisements: L. Siegel, Kurfürstendamm 237, D-1000 Berlin 15, Tel. (030 882 1031, Telex 01-85411,
Springer-Verlag Berlin Heidelberg New York
Printed in Germany by Beltz Offsetdruck, Hemsbach/Bergstraße

Diese Ausgabe enthält eine eingeheftete Beilage vom Springer-Verlag, Berlin, Heidelberg, New York