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Effect of Electron Beam Irradiation on Structure and Properties of Styrene-Butadiene Rubber

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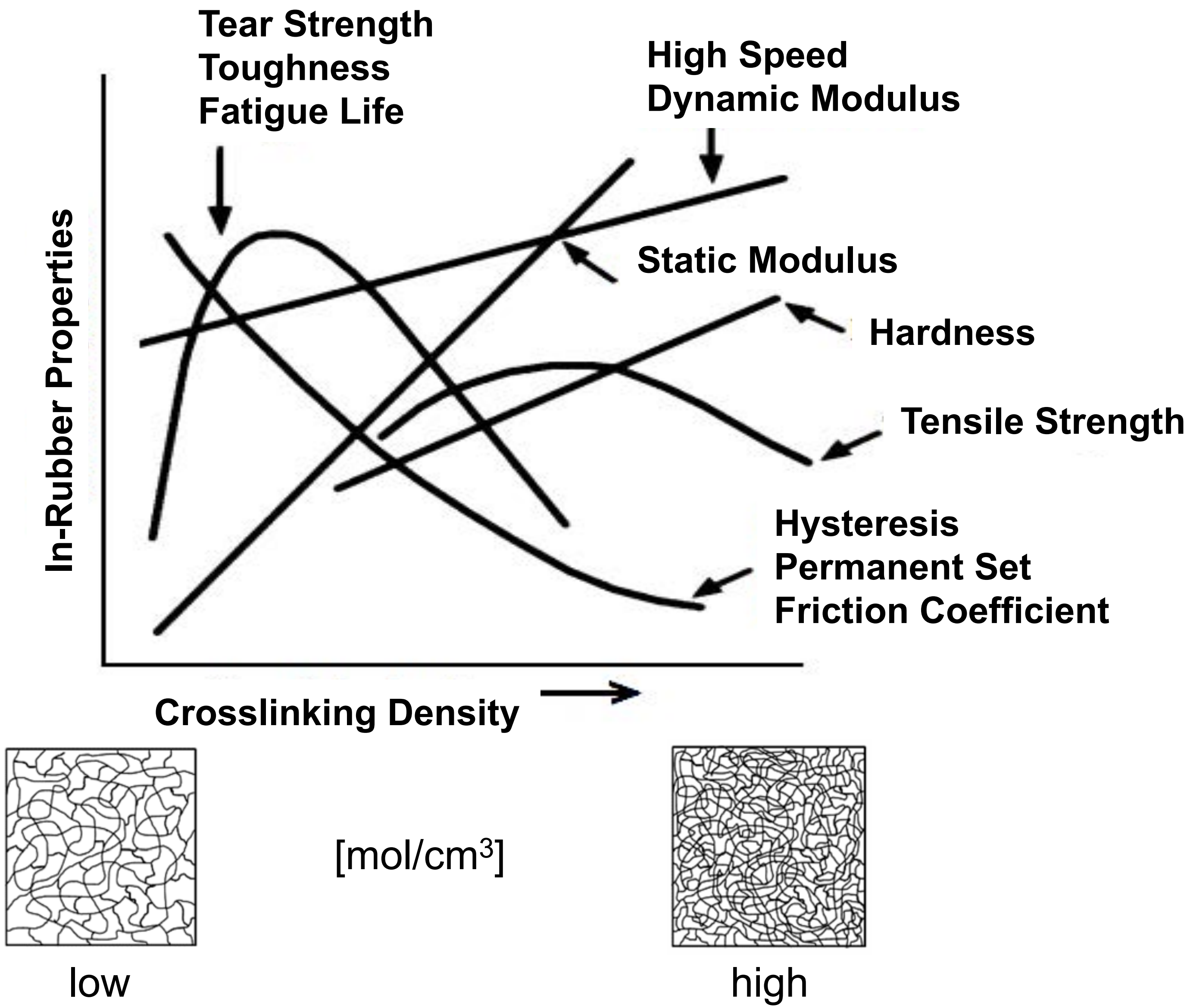
INTERNATIONAL RUBBER CONFERENCE (IRC), KUALA LUMPUR, 4th – 6th September 2018

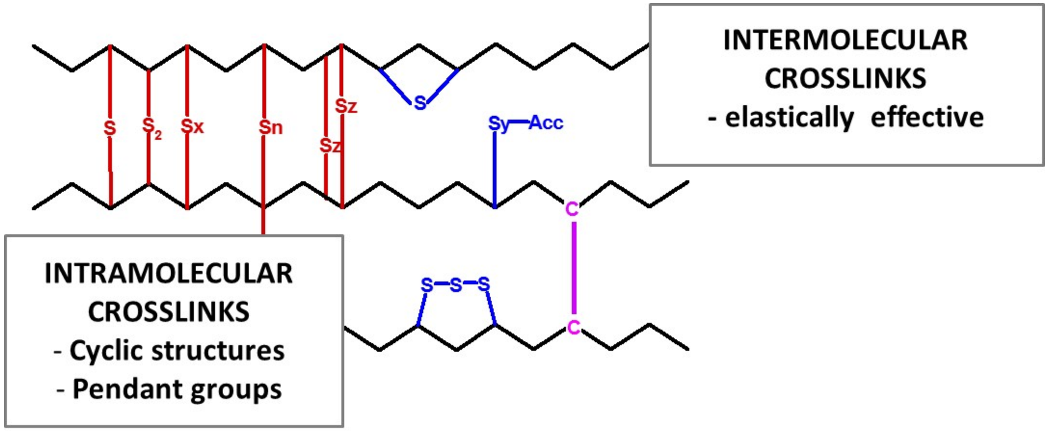
Crosslinking Density



Sulfur Curing

Disadvantage of sulfur curing:

- Presence of
  - double bond
  - Sulfur + accelerator in the compound
- 130 – 160 °C required 
- Variety in crosslinks



Peroxide Curing

Disadvantage of peroxide curing:

- Presence of peroxides in the compound
- 130 – 160 °C required

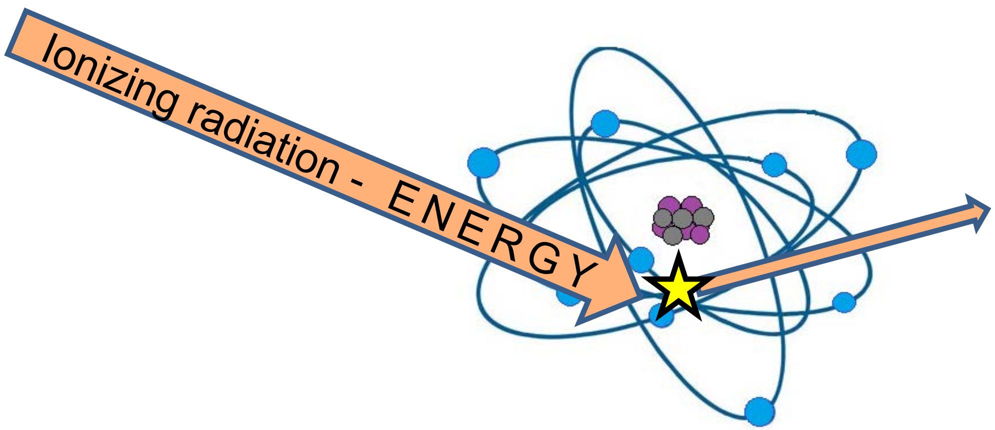
R-O-O-R’ ⟶ R-O* + *O-R’ + Heat

RO* ⟶ R* + O_2

Radiation Curing

Alternative crosslinking method: Radiation Curing

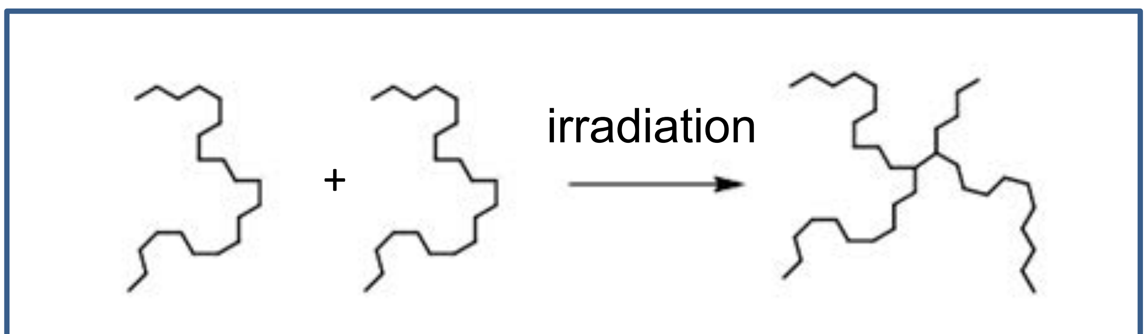
Electron beam – beam of high-energetic, accelerated electrons generated in electron accelerator



Radiation Curing

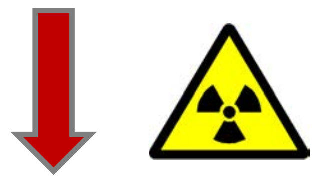
Alternative crosslinking method: Radiation Curing

- Independent of
  - double bonds
  - curing system
- Curing at room temperature is possible



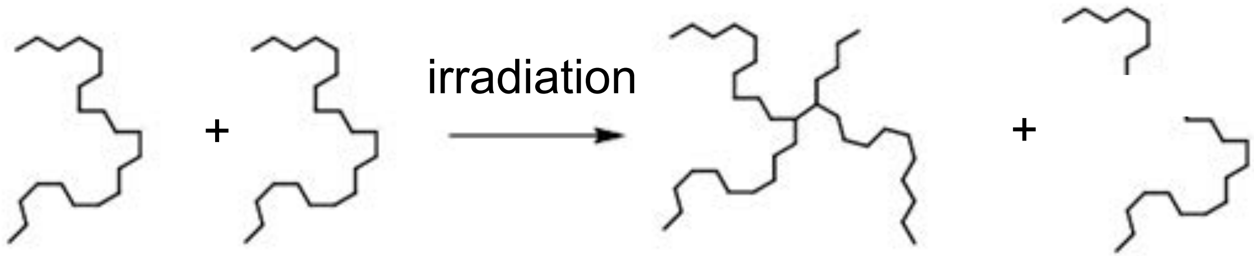
Radiation Curing

- Curatives are not necessary
- Process initiatated by high-energy ionizing radiation



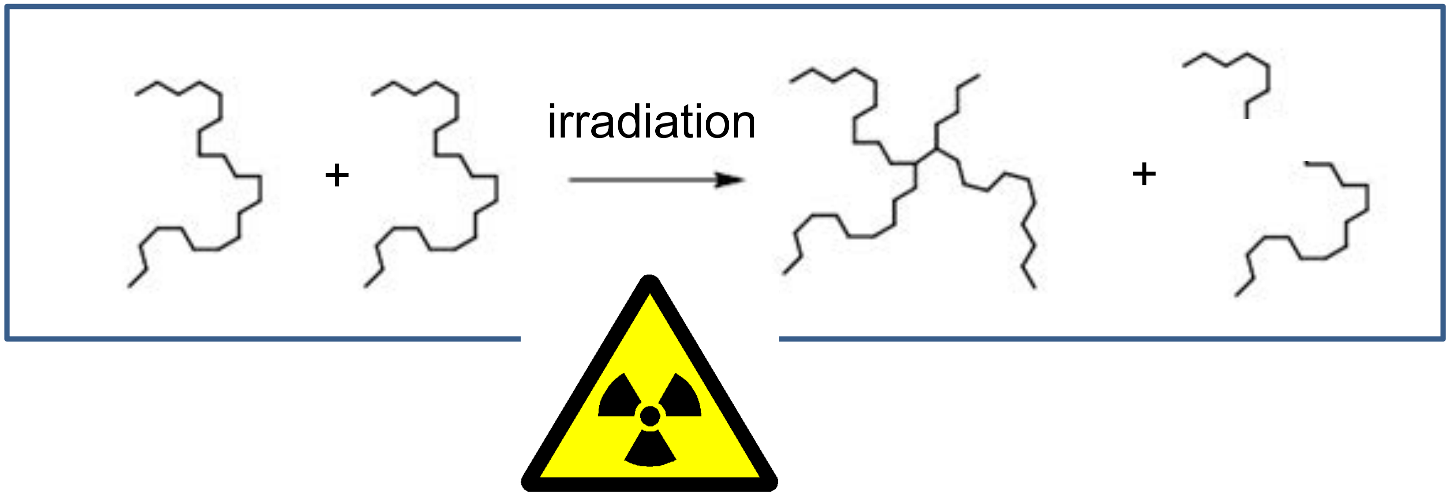
C-C crosslink between polymer chains

Degradation of the polymer



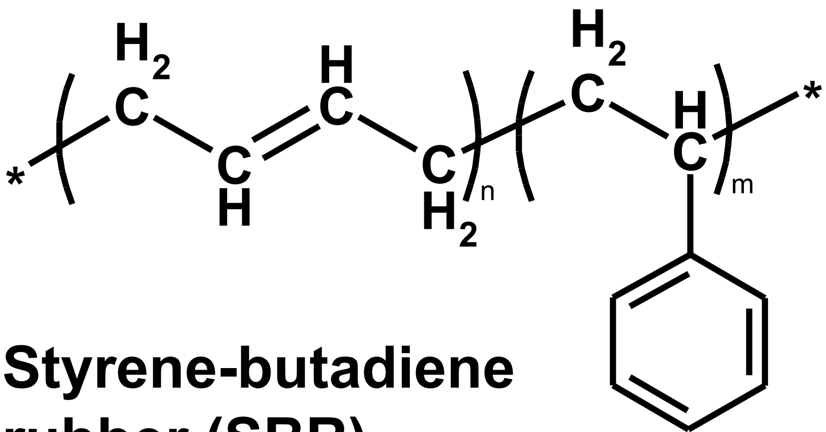
Radiation Curing

The higher the dose and power of radiation the higher crosslinking density.



But which radiation dose is the best for a good performance of the created network?

Radiation Curing



Styrene-butadiene rubber (SBR)

- E-SBR; KER 1500, Synthos (Poland); 23.5% of bound styrene
- $M_w = 425\,000\ g/mol$

- Irradiation with doses: **25, 50, 75, 100, 150, 200 kGy**
- Electron beam:
  - energy of 10 MeV
  - average power of 10 kW
- Irradiation conditions:
  - air atmosphere at room temperature

Reference sample: non-irradiated

Radiation Curing

Radiation curing leads to:

- C-C crosslink between polymer chains
- Degradation of the polymer

Charlesby-Rosiak tried to quantify both reactions by sol-gel analysis

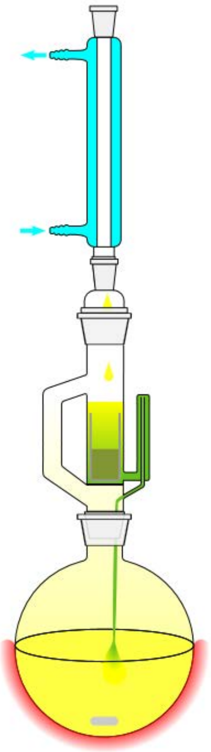
Sol-Gel Analysis

0,2 g rubber extracted with THF

(30 days) – drying at 60 °C (7 days):

→ insoluble (gel) fraction

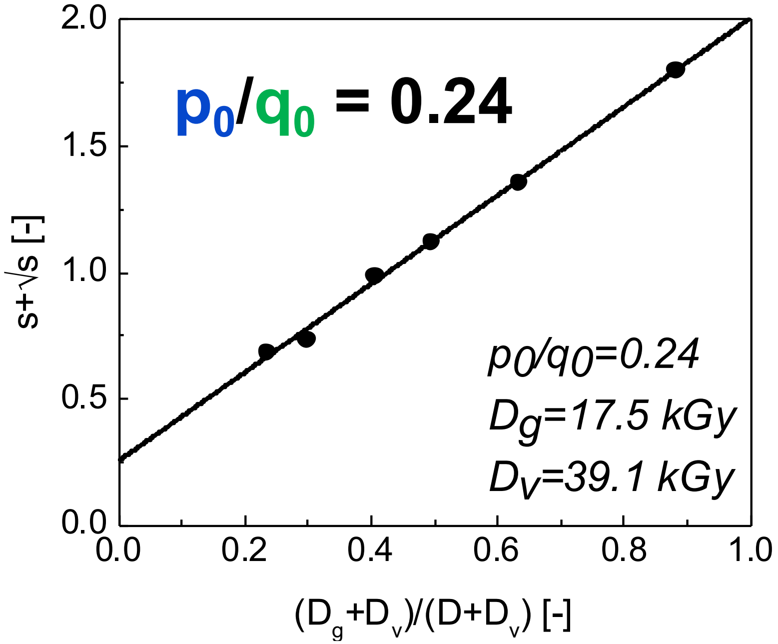
→ soluble (sol) fraction s



Soxhlet extractor

Chain scission vs crosslinking

Charlesby-Rosiak: $$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\left(\frac{D_v + D_g}{D_v + D}\right)$$



s – sol fraction

p_0 – average chain scission density per radiation dose unit

q_0 – average crosslinking density per radiation dose unit

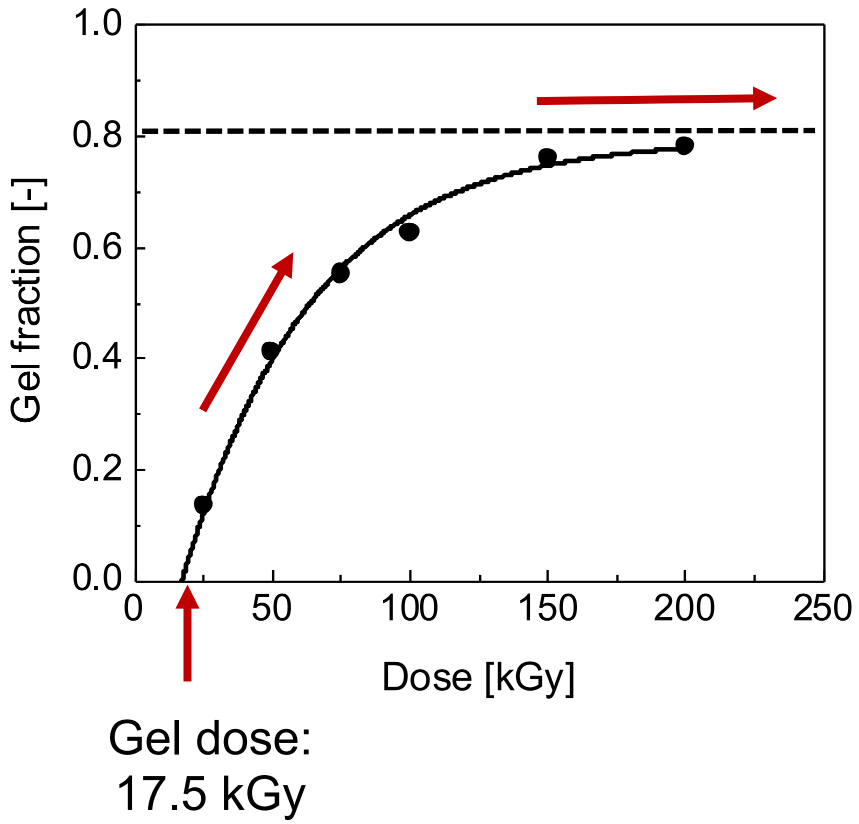
D – radiation dose

D_v – virtual dose

D_g – gel dose

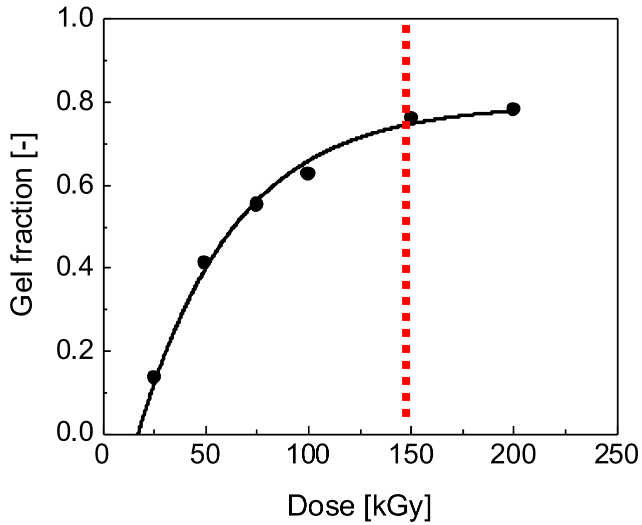
average chain scission density / average crosslinking density = ca. 1 : 4

Effect of ionizing radiation on gel formation: gel fraction

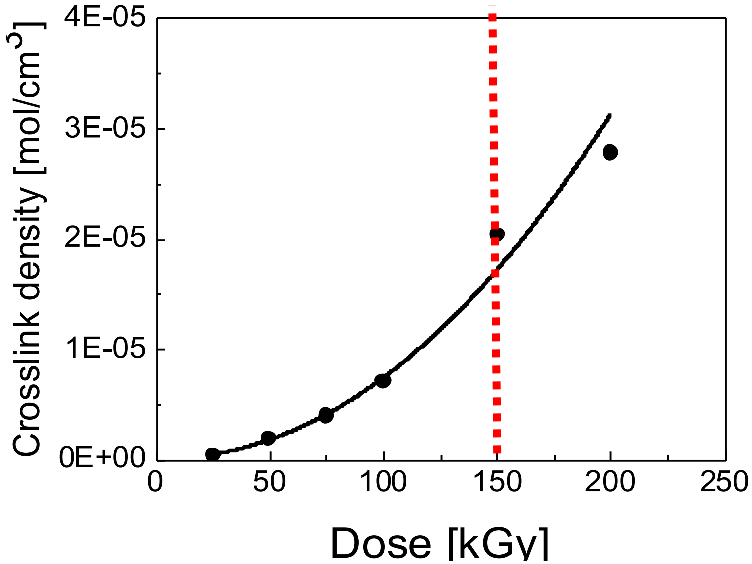


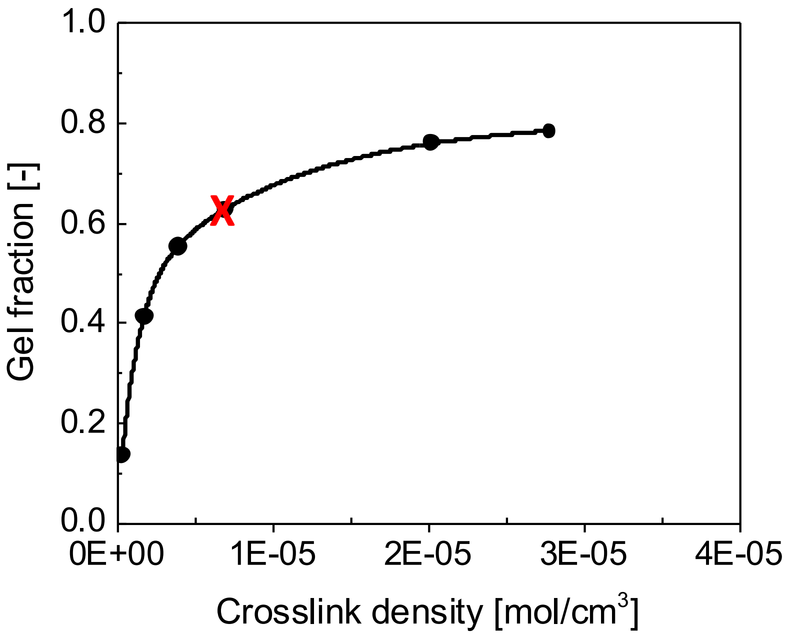
Higher irradiation leads to higher insoluble (gel) fraction - crosslink density

Gel fraction vs crosslink density



Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, calculation according to Flory-Rehner



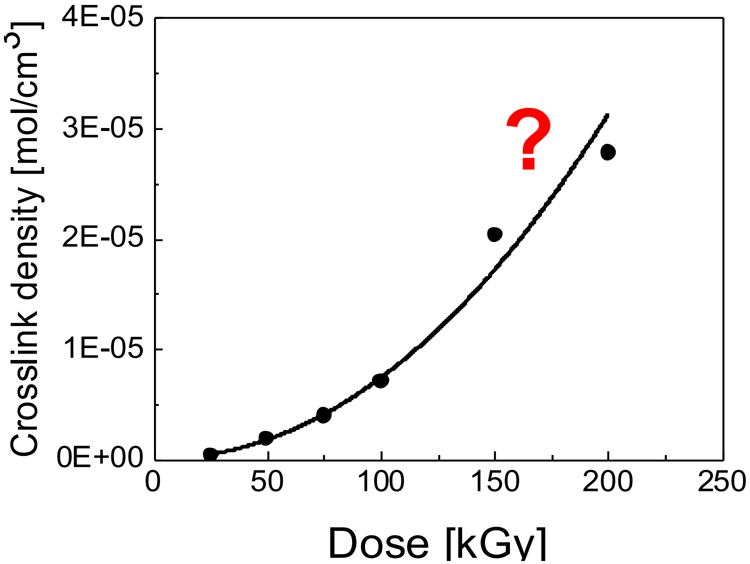


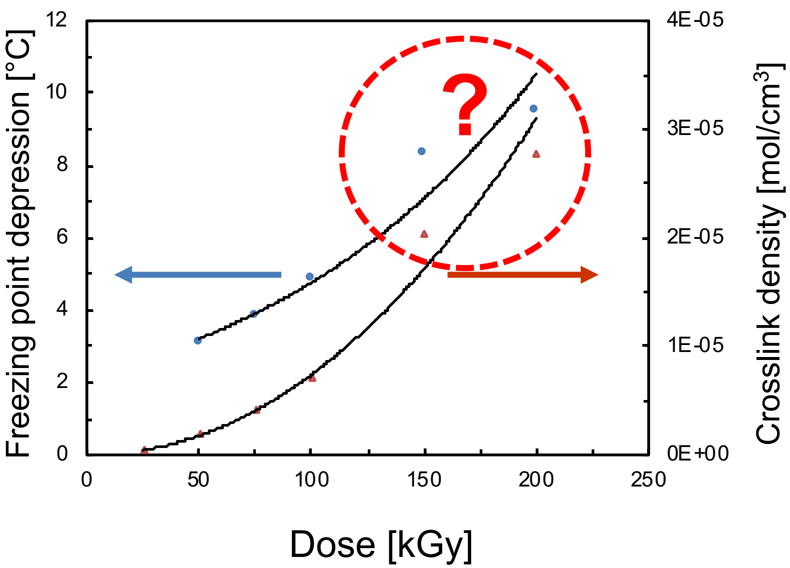
New chemical bonds are formed mainly between already crosslinked polymer chains at higher doses.

Crosslink density

Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, calculation according to Flory-Rehner

Samples swollen in toluene for 4 days at RT, dried 4 days at 60 °C, swollen in cyclohexane for 4 days at RT, **freezing point depression** evaluated by DSC (heating rate 5 K/min)

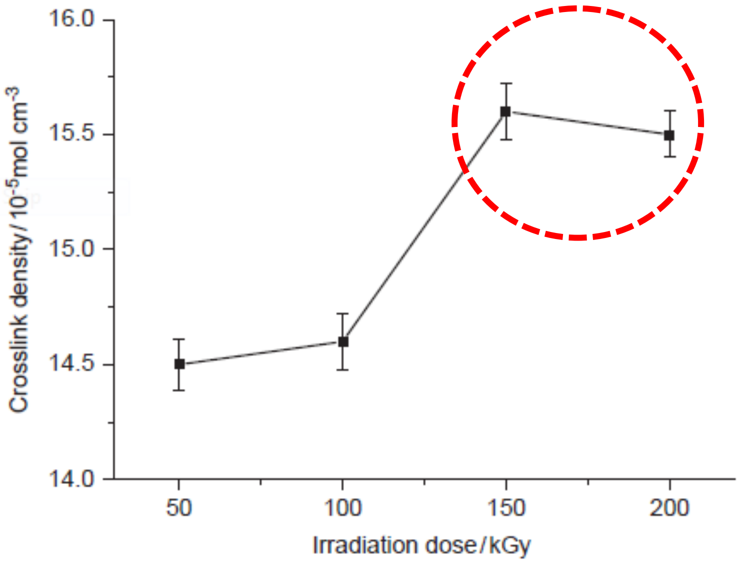


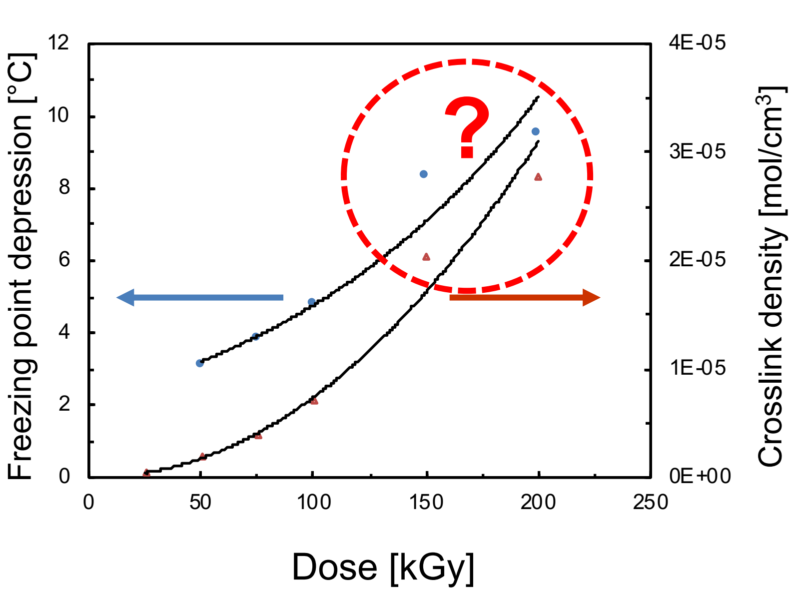


What happens at higher dosage rates?

Crosslink density

Q. Wang, Radiation Physics and Chemistry 78 (2009) 1001 – 1005: Influence on irradiation dosage on crosslinking density of E-SBR, measured by Magnetic Resonance Crosslink Density Spectrometer (MRCDS)





What happens at higher dosage rates?

Gel fraction vs crosslink density

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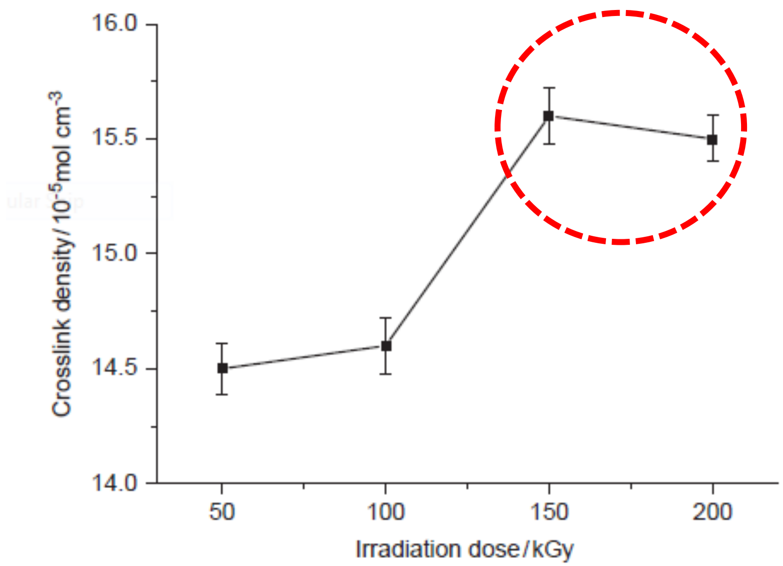
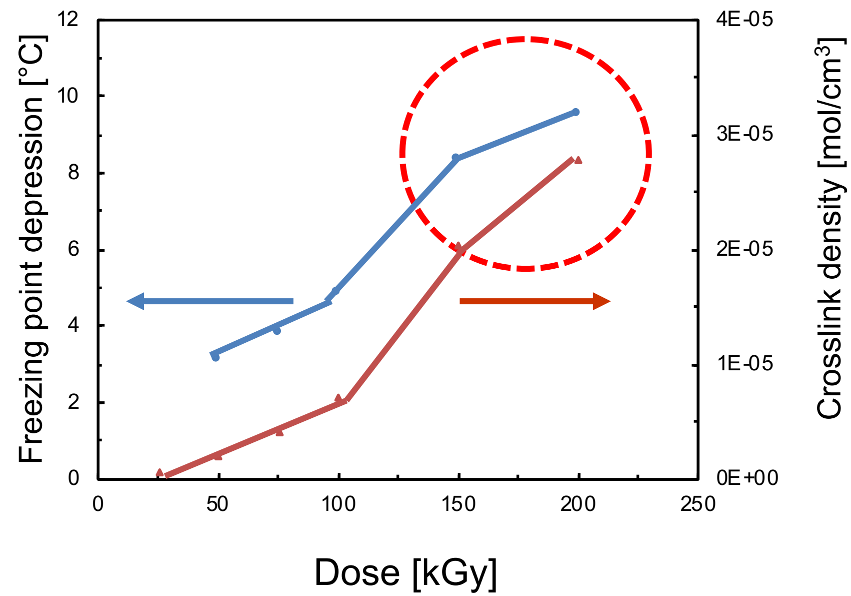
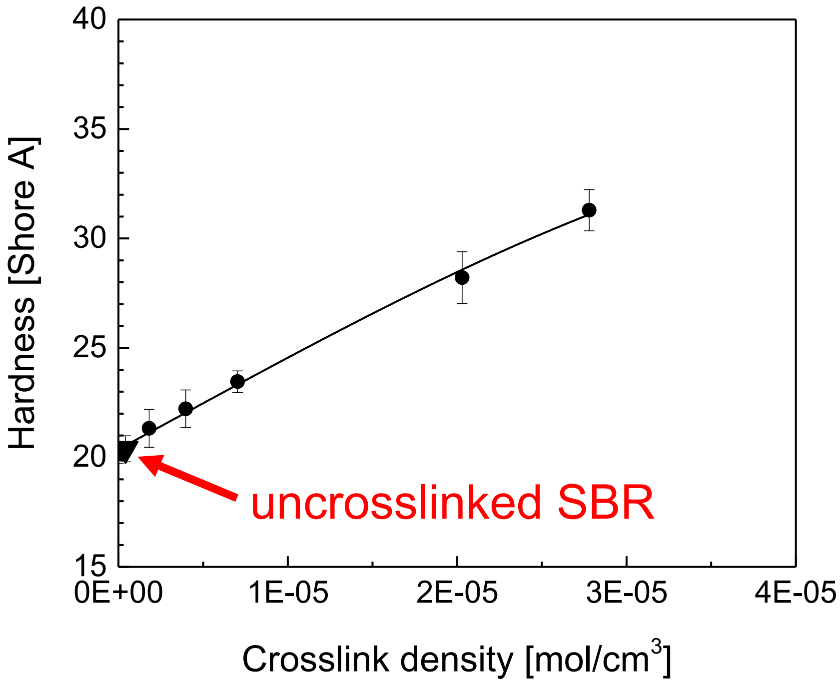


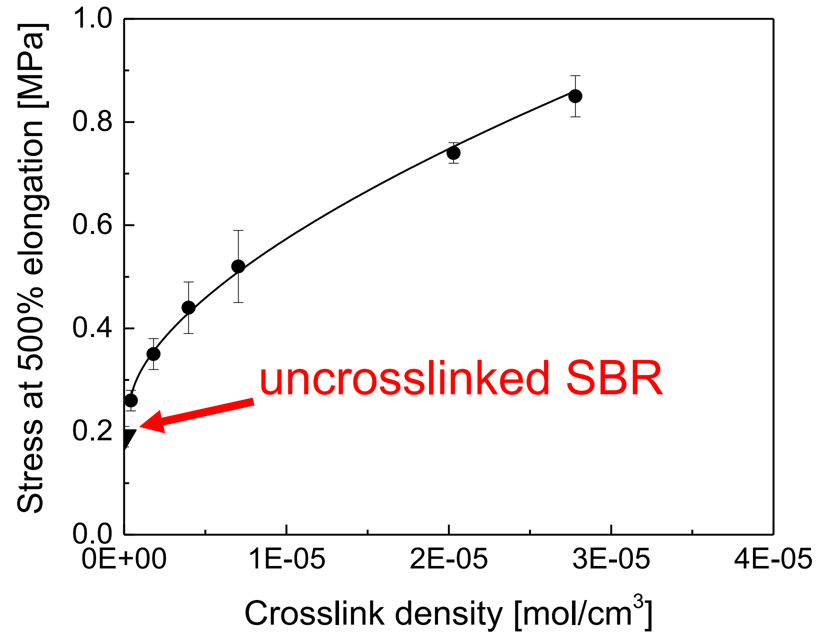


What happens at higher dosage rates?

Polymer degradation becomes more likely!

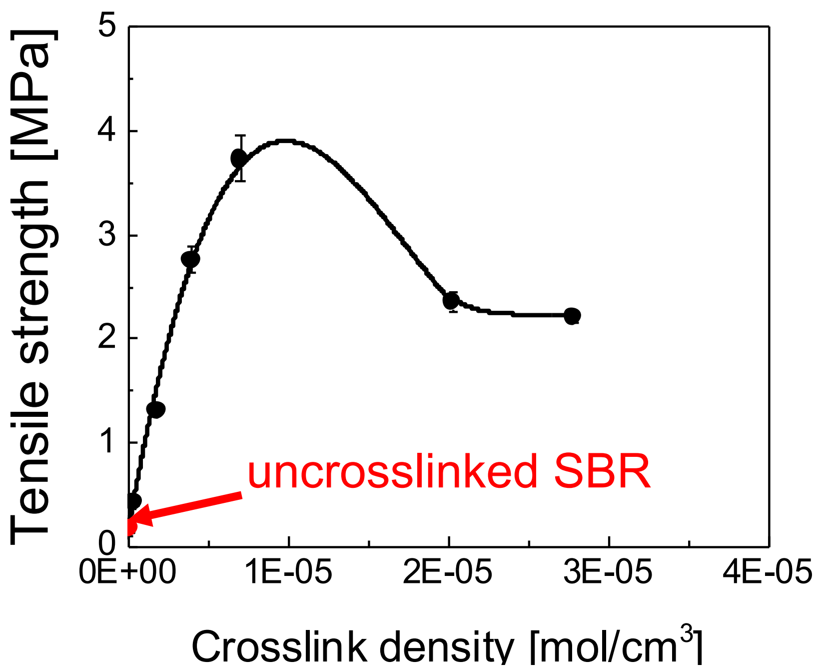
Effect of ionizing radiation on SBR structure: mechanical properties

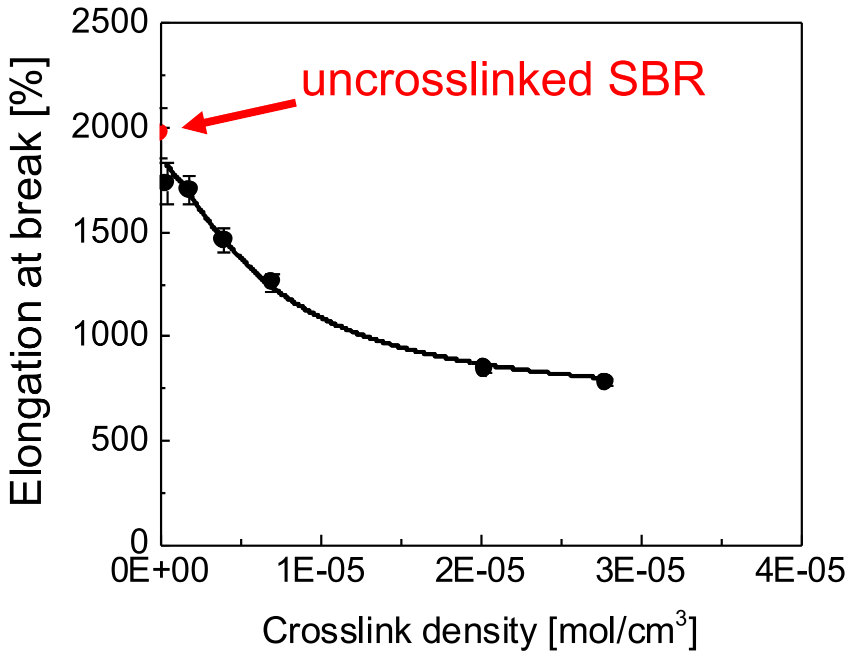




- Higher crosslinks lead to higher hardness
- Few crosslinks lead to significant increase in modulus

Effect of ionizing radiation on SBR structure: mechanical properties





- Maximum tensile strength: ca. for 100 kGy
- Few crosslinks lead to significant reduction of EaB

Summary

- SBR can be cured by radiation
- Radiation dose influences crosslink density
- Increasing crosslink density influences hardness and stress-strain behavior

Summary

Which radiation dose is the best for a good performance of the created network?

- Required radiation dose for sufficient SBR crosslinking network ca. 150 kGy
- Charlesby-Rosiak model is applicable for radiation-curing process
- Chain scission density / Crosslinking density = ca. 1 : 4

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Acknowledgements

Thanks to the Ministry of Science and Higher Education (Republic of Poland) for the financial support.

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Thank you for your kind attention!

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This paper is already published in:
Radiat. Phys. Chem. 2018, 149, 14–25 , DOI: 0.1016/j.radphyschem.2017.12.011

Radiation Curing

Radiation curing leads to:

- C-C crosslink between polymer chains
- Degradation of the polymer

1959: Charlesby and Pinner tries to quantify both reactions by sol-gel analysis

Sol-Gel Analysis

0,2 g rubber extracted with THF

(30 days) – drying at 60 °C (7 days):

→ insoluble (gel) fraction

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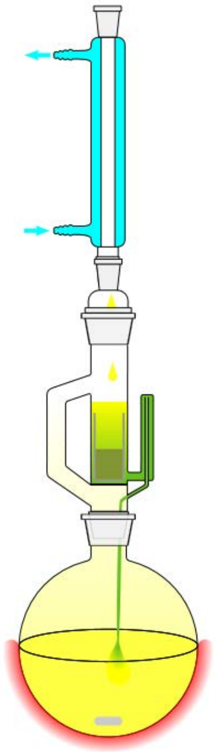


Soxhlet extractor

Sol-Gel Analysis

Charlesby-Pinner equation

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 u_{2,0} \boldsymbol{D}}$$

s – sol fraction

p_0 – average chain scission density per radiation dose unit

q_0 – average crosslinking density per radiation dose unit

$u_{2,0}$ – average degree of polymerization of the primary polymer chains

D – radiation dose

Charlesby-Pinner equation

Assumptions:

- Chain scission and crosslinking occur at random spatial distribution and proportionally to radiation dose
- Ratio between chain scission and crosslinking is constant over the whole range of doses
- Crosslinking leads to formation of tetra-functional crosslinks X, not tri-functional endlinks Y
- Initial molecular weight distribution is random:

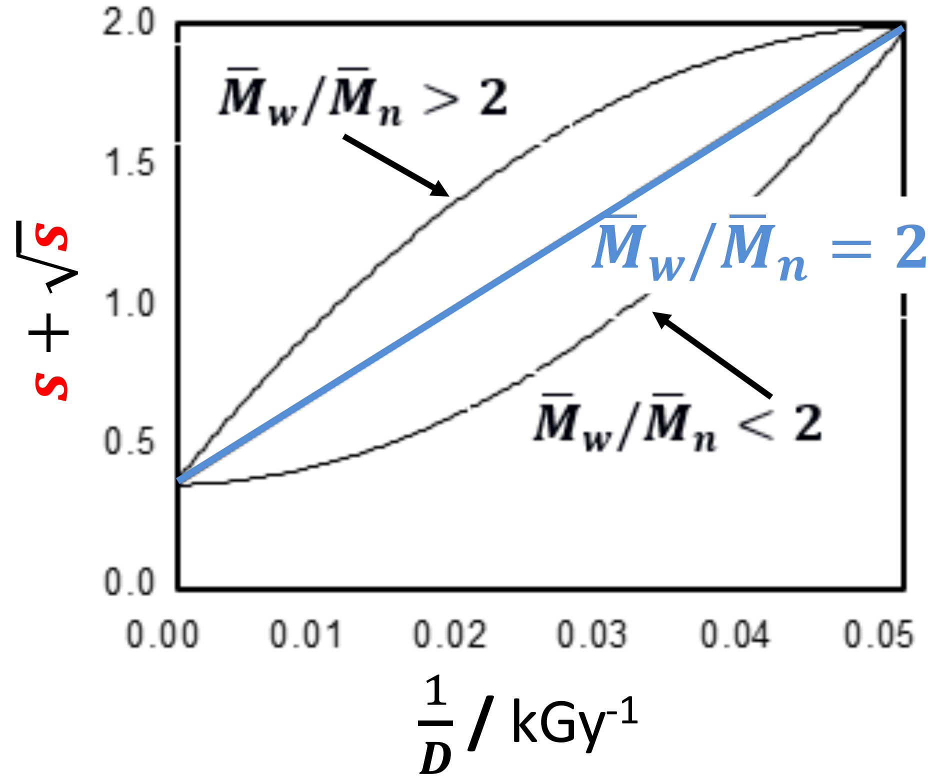
polydispersity index PDI = $\boldsymbol{\bar{M}_w/\bar{M}_n = 2}$

($\bar{M}_w$ - weight-average molecular weight

$\bar{M}_n$ - number-average molecular weight)

Chain scission vs crosslinking

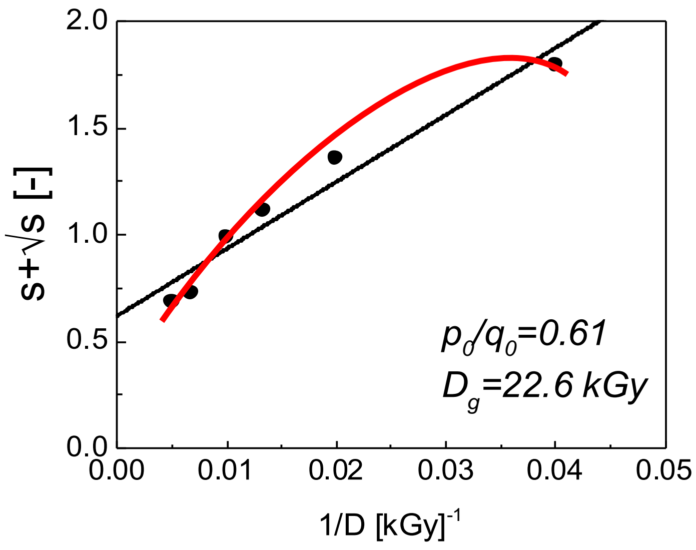
Charlesby-Pinner equation $s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 u_{2,0} \boldsymbol{D}}$



→ **Limitation of this model if $\frac{\bar{M}_w}{\bar{M}_n} \neq 2$**

Chain scission vs crosslinking

→ **Limitation of this model if** $\frac{\bar{M}_w}{\bar{M}_n} \neq 2$



Charlesby-Pinner equation

NO linear correlation!

$\bar{M}_w/\bar{M}_n > 2$

(GPC: PDI = $\frac{\bar{M}_w}{\bar{M}_n} = 2{,}8$ **)**

Chain scission vs crosslinking

→ **Limitation of Charlesby-Pinner if** $\frac{\bar{M}_w}{\bar{M}_n} \neq 2$

Charlesby-Rosiak equation

$$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\left(\frac{D_v + D_g}{D_v + D}\right)$$

s – sol fraction

p_0 – average chain scission density per radiation dose unit

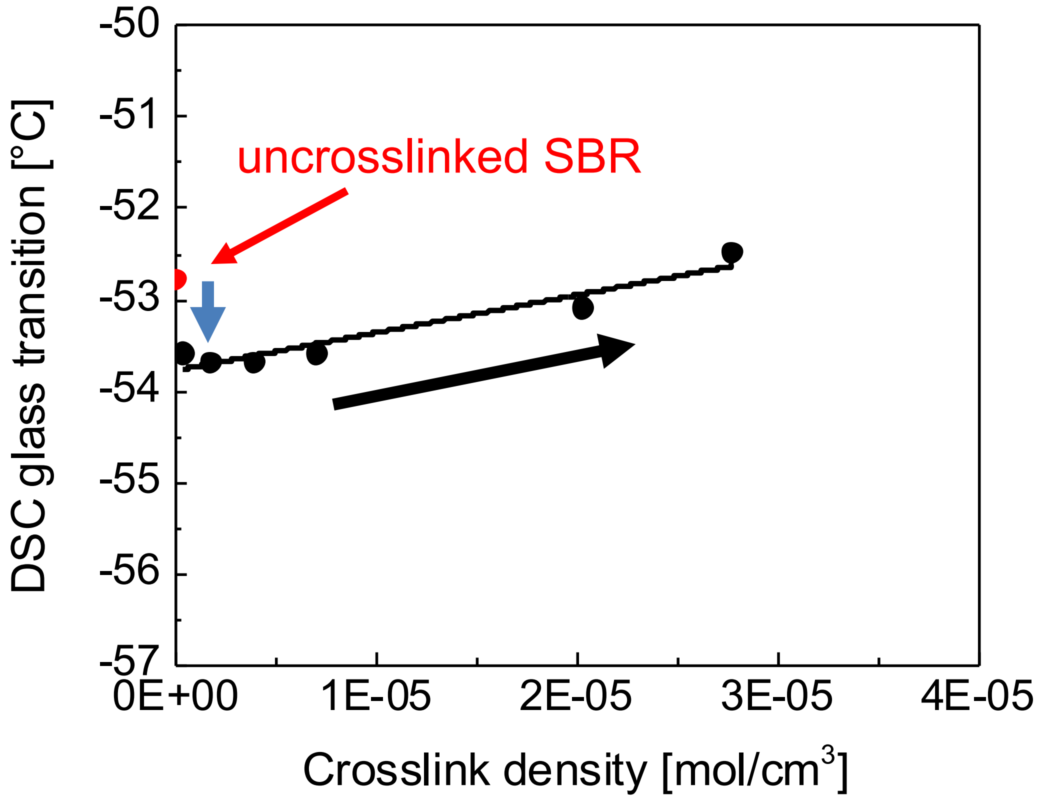
q_0 – average crosslinking density per radiation dose unit

D – radiation dose

D_v – virtual dose

D_g – gel dose

Effect of ionizing radiation on SBR structure: DSC glass transition temperature (T_g)



Decrease of T_g: chain scissions

Increase of T_g: formation of crosslinks

Yield of chain scission (G_s) and crosslinking (G_x)

Condition for effective crosslinking: $G_s/G_x < 4$

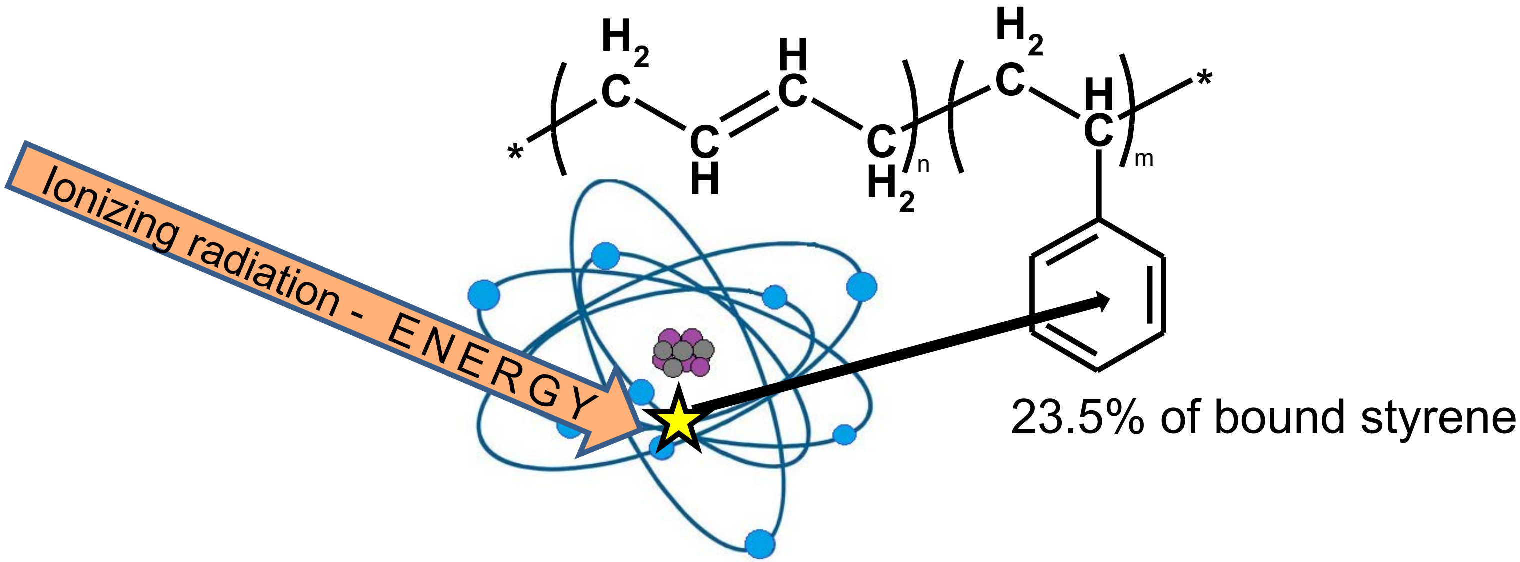
	G_s/G_x
Investigated **SBR**	0.49
cis-1,4 BR [1]	0.10
EPDM [2]	0.26

- **SBR, BR and EPDM can be crosslinked by irradiation**
- **Irradiation of SBR leads to higher chain scission than in EPDM or BR**

[1] Kozlov et al., Vysokomol. Soedin. A+, 11 (1969) 2230-2237
[2] Geissler et al., Macromol. Chem. Physic. 179 (1978) 697-705

Effect of ionizing radiation on SBR structure

Why does the irradiation of SBR leads to higher chain scission than in EPDM or BR?



- styrene ring absorbs radiation – dissipate it = more resistant to crosslinking but also to degradation
- styrene blocks stiffen the polymer chain = crosslinking is less likely

Influence of styrene content on crosslinking (G_x)

Used E-SBR; KER 1500, Synthos (Poland); 23.5% of bound styrene

	G_x in µmol / J [3]
SBR (16% of styrene)	0.30
SBR (28% of styrene)	0.16
SBR (85% of styrene)	0.03

Increasing amount of styrene hinders crosslinking.

[3] E. Witt, J. Polym. Sci. 41 (1959) 507-518