

NOTES

Influence of Chloroorganic Compounds on the Crosslinking of cis-Polybutadiene by ^{60}Co γ -Rays

INTRODUCTION

In the first publication¹ of this series—the influence of several conventional ingredients of rubber on the γ -radiation-induced crosslinking of polybutadiene was described. This influence is particularly marked in the case of chloroparaffin.

Following this conclusion the authors decided to examine more thoroughly the effect of chloroorganic compounds on the radiation crosslinking of *cis*-polybutadiene.

Experimental

The *cis*-polybutadiene rubber used in the present experiments, Europrene-Cis, consists of 92% *cis*, 2.2% *trans* and 5.8% vinyl configuration. Its weight- and number-average molecular weights are 227,000 and 131,000 respectively.

The mixtures of Europrene-Cis with chloroparaffin were prepared by milling. The chloroparaffin contained 67.5% chlorine and its weight-average molecular weight was 451.39. The samples prepared in the form of cylinders (10 mm in diameter and 6.3 mm in height) were deaerated and then irradiated by ^{60}Co -rays at a dose rate of 0.2 Mrad/hr. The deaeration was carried out in glass ampoules for 8 hr at 10^{-5} mm Hg. The density of crosslinking was determined by the method of equilibrium swelling of Flory and Rehner.²

The irradiated specimens were subjected to swelling in toluene, equilibrium being reached after 4–6 days. The constant of interaction between *cis*-polybutadiene and toluene was determined by osmometric measurements as 0.39.

In the next series of experiments *cis*-polybutadiene samples, about 0.5 g in weight were swollen in chlorohydrocarbon solvents up to 100% increase in weight and then irradiated in sealed glass ampoules. The deaeration was carried out as previously but at liquid nitrogen temperature. After the irradiation the samples were dried in vacuum at 50°C for 18 hr and subjected to the equilibrium swelling in toluene. The organic chlorides used in these experiments are enumerated in Table IV.

The irradiated and unirradiated samples, both in the presence and absence of chloroparaffin were subjected to IR analysis.

The changes of electric conductivity of *cis*-polybutadiene were measured before, during and after γ -irradiation. Using dc current of 100–400 V, the changes of the intensity of current were registered. The sample was placed in a steel mould, which acted as one of the electrodes. The second electrode was put into the center of the sample, which was then irradiated at a dose rate 0.6–0.7 Mrads/hr.

The samples of *cis*-polybutadiene and *cis*-polybutadiene with chloroparaffin for ESR measurements were irradiated in liquid nitrogen with the total dose of 2 Mrads.

Results and Discussion

The densities of crosslinking for varying content of chloroparaffin in polybutadiene irradiated with 7 Mrad dose are given in Table I and Figure 1.

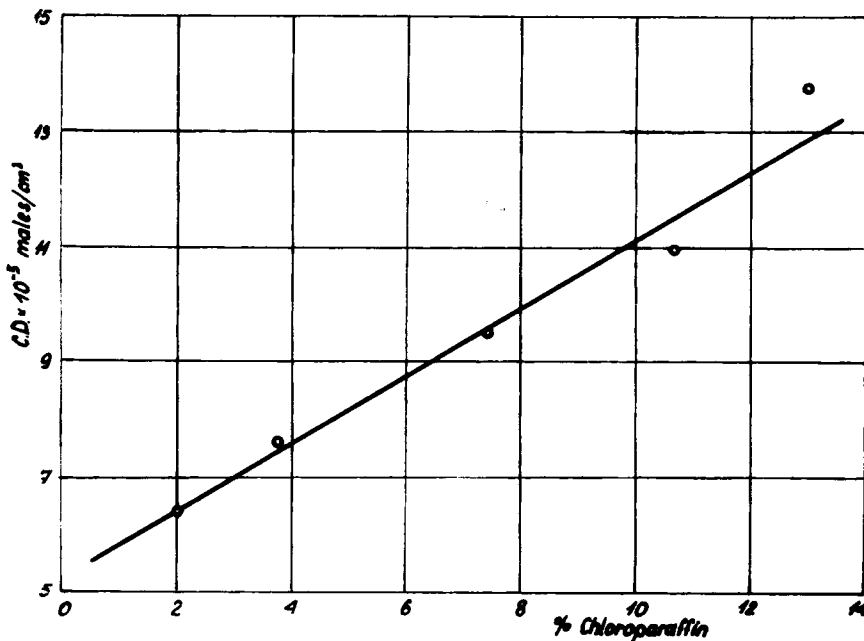


Fig. 1. Influence of chloroparaffin on the crosslinking density of *cis*-polybutadiene irradiated with 7 Mrad dose.

The density of crosslinking for polybutadiene, irradiated without additives, to 7.2 Mrad dose is only $2.82 \cdot 10^{-5}$ moles/cm³.

It may be seen that extent of radiation-induced crosslinking of *cis*-polybutadiene increases, in the investigated range, with increasing content of chloroorganic compound.

TABLE I
Crosslink Density of Polybutadiene Irradiated
in the Presence of Chloroparaffin (Total Dose: 7 Mrads)

% chloroparaffin added	Crosslink density × 10 ⁻⁵ , moles/cm ³
1.97	6.4
3.72	7.6
7.4	9.5
10.7	11.0
13.8	13.0

The influence of radiation dose on crosslinking of *cis*-polybutadiene in the presence of chloroparaffin is shown in Table II and Figure 2.

The density of crosslinking increases linearly with the radiation dose. The same type of dependence was observed by us previously for polybutadiene without additives.

Radiation yields of crosslinking are given in Table III.

Radiation yield for pure *cis*-polybutadiene, given already in the previous publication¹ is in good agreement with the value reported by Witt and Goodrich.³ Addition of chloroparaffin (7.4%) causes fourfold increase of the yield of crosslinking.

Chloroparaffin is completely inactive in thermal vulcanization, as has been proved experimentally by us.*

* Unpublished results.

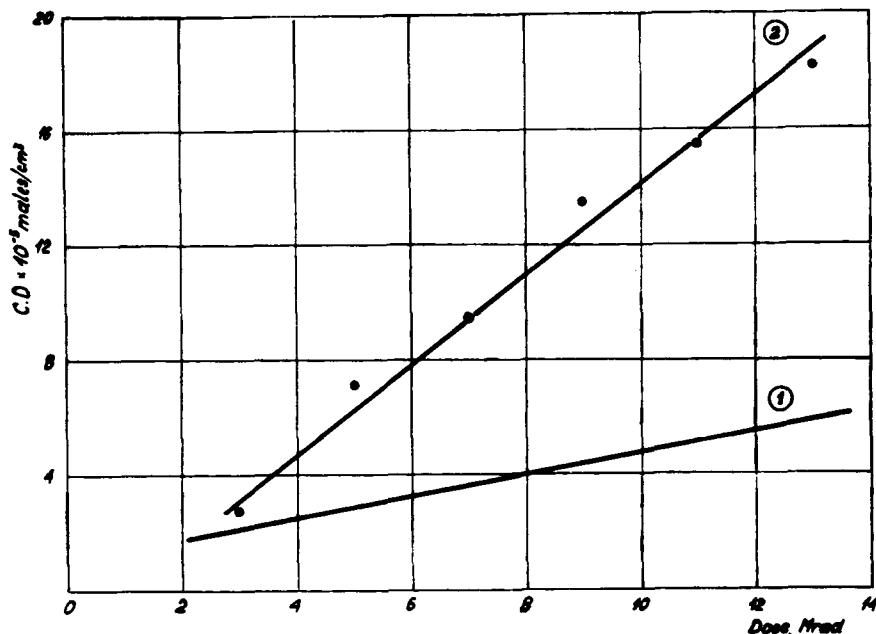


Fig. 2. Dependence of the crosslinking density of *cis*-polybutadiene on radiation dose (1) pure polybutadiene; (2) polybutadiene with 7.4% chloroparaffin.

The influence of some chloroorganic compounds on the radiation crosslinking of *cis*-polybutadiene is demonstrated in Table IV.

It seems that the greater the content of chlorine in chloroalkanes the larger is their accelerating influence on the extent of cross-linking.

TABLE II
Radiation Vulcanisation of *cis*-Polybutadiene
in the presence of chloroparaffin (7.4%)

Radiation dose, Mrad	Crosslink density × 10 ⁻⁵ , moles/cm ³
3	2.83
5	7.2
7	9.5
9	13.5
11	15.2
13	18.2

TABLE III
Radiation Yields of Crosslinking (Total Dose: 7 Mrad)

Irradiated material	Yield of cross-linkages/100 ev	Energy in ev/1 crosslinkage
Pure rubber	3.6	28.0
Rubber + chloroparaffin (7.4%)	14.0	7.1

TABLE IV
Influence of Organic Chlorides on Radiation
Crosslinking of Polybutadiene (Total Dose 4.4 Mrad)

Swelling agent	Content of chlorine in swollen rubb., wt.-% ^a	Crosslink density $\times 10^{-5}$ moles/cm ³
Isooctane	0.00	3.03
<i>n</i> -Butyl chloride	19.00	5.18
Chloroform	44.45	5.58
Carbon tetrachloride	46.00	6.13
Trichloroethylene	40.38	8.50
Pentachlorocyclopentadiene	37.05	9.50

^a Swelling was carried out up to 100% increase in weight.

More active seem to be chloroalkenes (trichloroethylene and pentachlorocyclopentadiene). The double bond in neighborhood of chlorinated carbon probably increases the efficiency of the compound in respect to crosslinking.

Chlorine trapped in *cis*-polybutadiene was determined after extracting the irradiated samples with acetone by Schöniger's method,⁴ whose accuracy is $\pm 0.3\%$.

The content of chlorine trapped in irradiated rubber was less than 1%, e.g. for *n*-butylchloride: 0.07%, for carbon tetrachloride: 0.66%.

Literature data⁵⁻¹⁰ on the radiolysis of chloroorganic compounds used in these experiments indicate that the relatively large quantity of chlorine in the rubber crosslinked in the presence of carbon tetrachloride may be due to the numerous radical and ionic products (CCl_2^+ , CCl_2^- , Cl^+ , Cl^-), which besides scavenging electrons, probably react directly with the polymer. On the other hand the radiolysis of *n*-butylchloride proceeds by different mechanisms (eg, isomerisation⁶) and therefore its participation in crosslinking is less significant. Consequently the content of chlorine bound with the polymer is lower. The IR analysis indicates that in the first period of radiation induced crosslinking the number of double bonds in *cis*-polybutadiene markedly decreases. This decrease is slightly larger in the presence of organic chlorides.

In the further stage of irradiation (crosslink density $10^{-5} - 10^{-4}$ mole/cm³) the number of double bonds does not change. This may be due to the addition of radiation produced radicals to the double bonds, but only as long as they are easily accessible.

In the presence of chloroparaffin additional number of radicals is produced as we have found by EPR measurements.

Consequently the decay of double bonds is faster. The presence of chloroparaffin does not affect the radiation induced changes of *cis*, *trans* and 1,2-configuration.

It was found, that in the γ -field the electric conductivity of *cis*-polybutadiene increased about 4.5 times and the conductivity of polybutadiene containing chloroparaffin (6.5%) increased 4.1 times. It is possible that chloroparaffin decreases the mobility of charge carriers in the irradiated polymer.

The above mentioned EPR and conductometric measurements seem to indicate that the radicals formed in the rubber in the presence of chloroparaffin may be produced from the molecules excited in ion recombination processes.

The results listed in Tables I-IV and demonstrated in Figures 1-2 show that direct addition of chloroorganic compounds in the course of crosslinking of *cis*-polybutadiene is insignificant. The amount of chlorine bound chemically with the rubber is very small indeed and furthermore fairly large differences in the contents of chlorine (Table IV) in the solvent do not lead to marked differences in the crosslinking density.

Further experiments are intended to explain the contribution of ionic and radical processes to the observed phenomena.

References

1. B. Jankowski and J. Kroh, *J. Appl. Polym. Sci.*, **9**, 1363 (1965).
2. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943).
3. E. Witt and B. F. Goodrich, *J. Polym. Sci.*, **41**, 507 (1959).
4. W. Schöniger, *Microchim. Acta*, 123 (1955); 869 (1956).
5. T. H. Chen, K. Y. Wonk, and F. J. Johnston, *J. Phys. Chem.*, **64**, 1023 (1960).
6. W. Cooper and W. H. Stafford, Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Vol. 29, Geneva 1958, p. 118.
7. E. B. Disumees and W. S. Wilcox, *Radiation Res.*, **11**, 754 (1959).
8. J. W. Schulte, *J. Am. Chem. Soc.*, **79**, 4643 (1957).
9. W. Miller, W. H. Stafford, W. H. Taylor, D. Laaver, and A. H. McQuillan, *J. Chem. Soc.*, 4485 (1961).
10. A. Robalewski and W. Zieliński, *Przem. Chem.*, **43**, 318 (1964).

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