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STUDYING THE ROLE OF DISULFOCHLORIDE BENZENE IN UNSATURATED ELASTOMERS

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Abstract: It has been studied the role of disulfochloride benzene in unsaturated rubbers (cis SKB, SKN-26) in the systems of SKB+disulfochloride benzene and SKN-26+disulfochloride benzene with radiation exposure. It has been showed the changes in the molecular structure of rubber after irradiation with γ -rays by 300 kGy by radiation dose by the physical, chemical and spectral methods. It has been defined the outputs and the emergence of cross-linking in elastomers for each of the system depending absorbed on the dose. It has been suggested that the mechanism of radiation heterogeneous transformation of elastomers in the presence of disulfochloride benzene.

Keywords: *butadiene-nitrile rubber, cross-linking, radiation, sensitizier, polyfunctional monomers.*

1. Introduction

Cross-linking of unsaturated elastomers is one of advanced methods that have a predetermined set of properties. To use this method you need to know the basic patterns of change in physical and chemical properties during cross-linking of different polymer macromolecules in the system. The emergence of cross-linking in copolymers with new properties can be associated not only with the act of linking, but also with structural changes that occur as a result of this reaction [1-10].

To characterize the structure of polymers- it has the value of the spatial grid density. It is known that to achieve the optimal properties of elastomers, a fairly large doses are required, which increases the cost of material. The introduction of some low molecular weight compounds can reduce absorbed dose without compromising the basic properties of the rubber [11-17, 24-26].

The solid fine powder low molecular weight organic sensitizers were practically applied [6, 7, 17, 23, 24]. In this regard, the sensitization and radiation cross-linking of unsaturated elastomers are actual. However, the parameters of cross-links of unsaturated elastomers in the presence of disulfochloride aromatic compounds derived by radiation-chemical method are almost unexplored.

In this paper we presented data about the process of radiation cross-linking of unsaturated elastomers in the presence of disulfochloride aromatic compounds, which is of significant interest because of its high efficiency as a sensitizing and cross-linking agent.

2. Experimental

The object of the investigation was unsaturated butadiene-nitrile rubber (SKN-40) obtained by the emulsion polymerization[2], as a sensitizing cross-linking agent it was used disulfochloride benzene (DSCB) [18,20,22] which is obtained by the interaction of benzene with an excess of chlorosulfonic acid [8].

Dissolution DSCB in the elastomer was performed by mechanical plastification method on rolls. After through mixing for 3-5min it was prepared polymer binary heterogeneous mixture containing 100 mass part of rubber and 8 mass part of DSCB.

Radiolysis of binary mixtures carried out by γ -rays of Co^{60} at dose 6.9 Gy/s. The calculation of the absorbed dose of the researched object was conducted by the method [9]. Samples weighing 1g were placed in glass vials ("Ray") and evacuated to a residual pressure of $1,33 \cdot 10^{-2}$ Pa.

The characteristic viscosity of irradiated binary mixtures (1, 2) was determined in toluene at 293 K by known method on the viscometer type Ubbelohde at the constant $K=4.9 \cdot 10^4$ and $X=0.64$ (for toluene) [10]. For quantitative characteristics of the spatial grid of the irradiated samples it was used the following parameters: the number of chain grid $1/M_c$ and the number of cross-linked molecules $1/M_{nr}$ in the rubber (mol/sm^3).

The determination of these parameters were conducted by the sol-gel analysis [10], which is based on sequential extraction of samples with solvents, first acetone and then toluene. The value of radiation-chemical yield (RCE) and the number of chain grid $1/M_c$ and the number of cross-linked molecules $1/M_{nr}$ was calculated by the equation of Flory-Rehner [11].

By IR spectroscopy method it was determined the change of molecular structure of the irradiated cross-linked rubber with the presence of DSCB. Irradiated rubber system (1, 2) was dissolved in toluene during 48h. Rubber films were prepared by coating solution to substrate and a constant evaporation of the solvent. As a substrate it was used windows from KBr material. During the measurement of spectrum at range of $700\text{-}2200\text{cm}^{-1}$ and windows of LiF and NaCl at range of $2000\text{-}4000\text{cm}^{-1}$, in order to avoid oxidation, the film was dried to constant weight in vacuum desiccator. Substrate with film was mounted in a holder and placed in the sample compartment of the spectrophotometer. The spectra of cross-linked samples were recorded before and after irradiation.

Obtain of free radicals in the irradiated samples occurred by study of mixtures of the spectrometer RE-1306 at a low temperature 77K in vacuum. Samples were prepared quickly submerged vials in liquid nitrogen, in which they were in further experiments and measurements. As reference changing of EPR spectra of determining g-factors and line widths used ions of Mn^{+2} of MnO. Identification of IR and EPR spectra were carried out in accordance with the correlation tables [12-14].

3. Results and discussion

As results of the research show an interaction of DSCB occurs with molecules of cis-butadiene and butadiene-nitrile rubbers at 100 kGy dose, leading to the formation of three-dimensional grid as evidenced by growth of the number of cross-links (N_c) and the number of cross-linked molecules $1/M_{nr}$ (Figure 1) with increasing doses of irradiation. Elastomers in the absence of a cross linking agent under the same conditions are not sewn (SKB) or sewn into a very small extent.

Fig.1 shows the data on changes of characteristic viscosity in the systems of SKB+DSCB, SKN-40+DSCB depending on the dose of irradiation. It follows that in both systems the viscosity increases monotonically at low doses (100kGy). With the increase of the absorbed dose the molecular weight of rubber increases. The characteristic viscosity increases from 0.3 to 0.9 for system SKB+DSCB and for the system of SKN-26+DSCB from 0.5 to 1.2. With the increase of the absorbed dose to more than 500kGy the characteristic viscosity decreases.

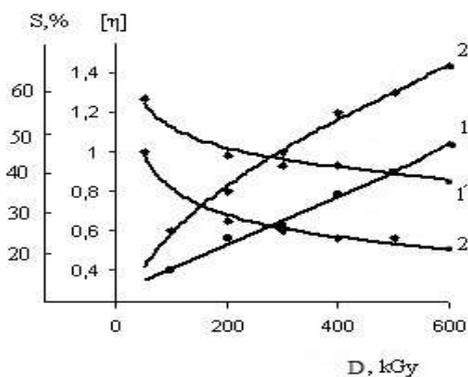


Fig.1 The dependence of characteristic viscosity of rubber (1- cis-SKB+DSCB; 2-SKN-26+DSCB) and the content of the sol fraction (1'-cis SKB+ DSKB; 2`- SKN-26+DSCB) from the irradiation dose in the sample.

The decrease of molecular weight of rubbers occurs by destruction of macromolecules of polymer. Increase of viscosity at the range of values during sensitizing at dose 400-500 kGy may be related with formation of spatial structures as a result of intramolecular cross-linking reactions.

The number of soluble sol fraction of the rubbers at irradiation doses 200kGy is achieved for both the rubbers at the range 50-30% and at doses 400-500 kGy irradiated polymer becomes completely insoluble, indicating about cross-linking of the molecules of polymer chains. Consequently, the increase in molecular weight of rubber observed during irradiation is carried out with vinyl links located in the position to the 1 and 2 [5,6,19,27]. The formation of effective cross-links occurs at doses 200kGy with low rates. Furthermore, this rate increases with the dose in systems SKB+ DSCB (1) and SKN+DSCB (2). At dose of 300 kGy, the number of effective cross-links in the system 1 is $4,1 \cdot 10^5 \text{ mol/sm}^3$, and in the system 2 is $9,2 \cdot 10^5 \text{ mol/sm}^3$ (Figure 2). From the data presented in Figure 2 the data show that irradiation of (SKB+DSCB; SKN +DSCB) cross-linking increases slightly.

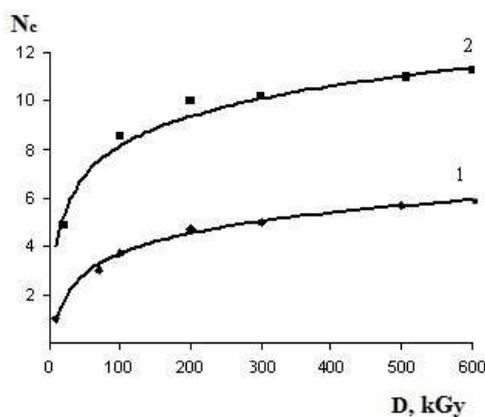


Fig.2 Dependence of number of cross-links (N_c) on irradiation dose of cis-butadiene (1) and nitrile butadiene (2) rubbers with DSCB (3 mass part per 100 mass part of rubber).

From the Fig 2 it is obvious that during irradiation of system (SKB+DSCB; SKN+DSCB) the cross-linking increases insignificantly. In the irradiated system SKN-26+DSCB the rate of cross-linking is higher than in the cis- SKB+DSCB. This is explained by the fact that in SKN-containing 1.4 trans-isomers higher. The nature of the interaction rubbers with DSCB was judged by change in IR-spectra (Figure 3)

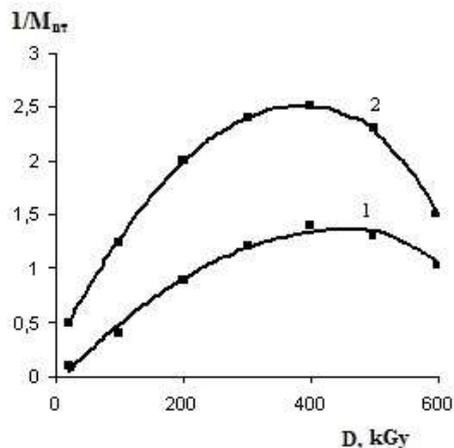


Fig.3 Dependence of number of cross-linked molecules per one cross-link ($1/M_{nt}$) on the dose of cis-butadiene (1) and nitrile butadiene (2) rubbers with DSCB (3 parts of DSCB by mass per 100 parts of rubber).

After irradiation of films in the case of both rubbers the intensity decreases after absorption at 1360 , 1195 and 1170 cm^{-1} characteristic for the group $-\text{SO}_2\text{Cl}$, as well as the emergence of a new band at 1150 cm^{-1} related to sulfonyc group $-\text{SO}_2$ [12]. And in either case there is a reduction of maximum intensity at 1650 cm^{-1} , characteristic for vibrations of the $-\text{C}=\text{C}-$ groups (figure 4).

In cis-butadiene rubber it is observed cis-trans isomerization of polymer molecules by the influence of DSCB, that is evidenced by the increase in optical absorbance band at 967 cm^{-1} , characteristic for $\text{CH}=\text{CH}$ trans configurations and a decrease in optical absorbance band at 730 cm^{-1} , associated with fluctuations CH groups in the cis position [12,13].

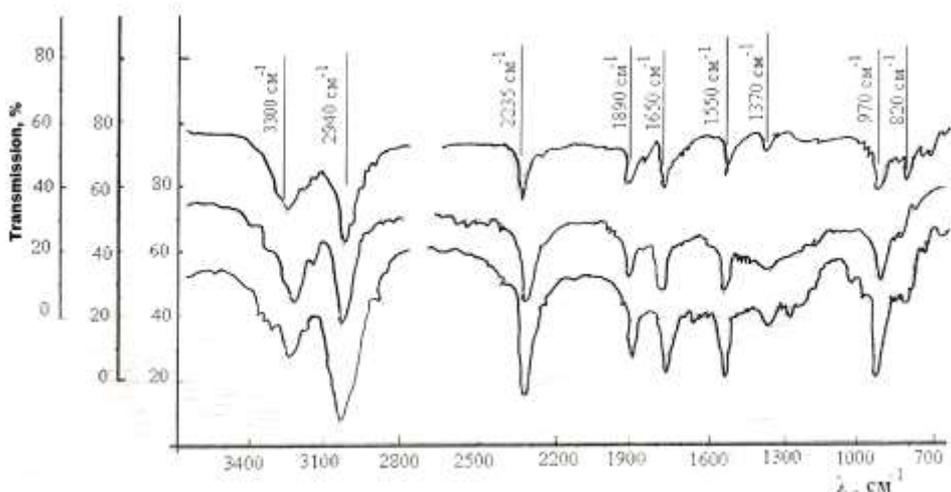


Fig. 4 The IR spectra of unsaturated elastomers (cis-SKB, SKN-26) with sensitizer 8 mass. Part of disulfochloride benzene after dose 500kGy.

a) row SKN-26; b) irradiated SKN-26+DSCB; c) irradiated cis-SKB+DSCB.

For the system of butadiene-nitrile rubber + DSCB by pull of the active chlorine from the sulfochloride groups there is a chemical interaction between sensitizing agents with double bonds of the polymer. Formed cross-links contain - SO₂ - group.

It is known that radiation cross-linking of unsaturated elastomers with aromatic chlorinated compounds is activated by metal oxides [2,3]. For confirmation of the assumptions about the direction of the reactions of SKN-26 with DSCB by irradiation we occurred number of researches. By irradiation of different doses it was determined contents of total and combined chlorine in the samples containing DSCB and counted the number of molecules DSCB due to the formation of one cross-link. The data presented in the table 1 show that for DSCB with increasing dose the amount of total chlorine increases. Also increasing the amount of chlorine, which came into reaction with zinc oxide with the formation of chlorides and, finally, to join DSCB elastomer molecules. That confirmed with the fall the content of DSCB in toluene extract till completely binding the cross-linking agent with the elastomer. The concentration of cross-links in the sample increases and the number of molecules per one DSCB cross-link is reduced with increasing dose.

Table1. Influence of DSCB to the chemical composition of elastomers SKN-26 and Cis-SKB, which content 5,0 parts of Zink oxide by radiation influence.

Cross-link system Mass part to 100 mass p. of elastomers	Dose, kGy	Chlorine content in sample, %			Content of DSCB in extract, % to conducting	Yield of number of cross- links, G	Number of cross- linking molecules per cross- links
		General	Related	Including ZnCl ₂			
100 3,0 5,0	250	85	16.1	4,7	9.8	3,8	1,27
SKN-26+ DSCB + ZnO	500	63	50.8	11,3	trace	5,3	0,91
100 3,0 5,0	250	85	14.2	3,1	6.9	2,6	0,97
SKB+ DSCB + ZnO	500	59	46	9,0	trace	3,5	0,68

Measurements show that with increasing doses the gel fraction content increases significantly in both systems. The formation of the insoluble fraction at low doses (sensitization) is higher in the SKN-26+DSCB+ZnO. The maximum gel content (80-90) in the cis-SKB and SKN-40 in the presence of DSCB suggests that DSCB participate in the process of sensitization and cross-linking.

Taking account into these facts, we can try to explain the position of radiated sensitizing agents in relation with the SKB-26 as follows: cross-linking of SKN-26 with DSCB at dose 300 kGy in the absence of zinc oxide is likely that during cross-linking of BNR with DSCB can participate tertiary carbon atoms from the parts of polybutadiene structures 1,2. However, we know that the number of chains of 1.2 for rubber SKN-40 is almost 10%. Therefore, it is known, that determining effect on the cross- linking has tertiary carbon atoms bound to the nitrile group.

Confirmation of radiation mechanism of the reactions, the growth of the number of cross-links (N_c) and cross-linked molecules (1/M_{nr}) at sensitization of unsaturated elastomers (cis - SKB, SKN-26) was found in studies of this system by detecting free radicals corresponding to EPR signal (figure 5).



Fig. 5 EPR spectrum of unsaturated elastomers with sensitizer DSCB irradiated by dose 500kGy in cold conditions 77K. 1. The spectrum of irradiated elastomer cis-SKB in the presence of 8 parts DSCB. 2. The spectrum of irradiated elastomer SKN-26 in the presence of 8 parts DSCB.

The electrons in all studied samples in the EPR spectrum are characterized by a narrow singlet line without a trace of fine structure at cold mode 77K. At the highest dose (500 kGy) in sensitized elastomer the signal intensity changes, there is a weak broadening of the appearance of a well-resolved spectrum of the radical in the form of two narrow singlet with width $\Delta H=1.3$ mT, ($q=2,0031$) and $\Delta H=1,1$ mT ($q=2,0031$). The observed phenomenon is probably related to the uneven distribution of radicals in the bulk samples. During radiolysis of polymeric systems containing electro acceptor polar groups involved in the course of the processes of electron capture by these groups. Positive and negative ions must react with the varied reactions of free radicals (Bellamy, 1980).

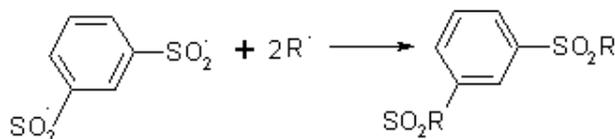
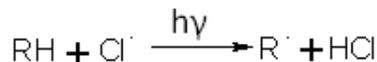
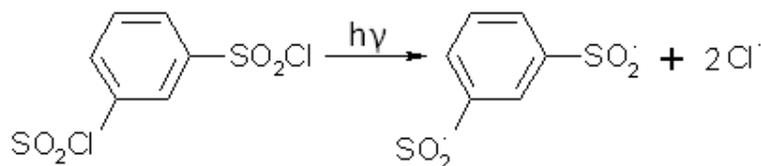
By studying the recommendation on addition of low molecular weight sensitizers (DSCB) into elastomer system we can do some conclusion on microstructures of the molecular chains of the elastomer.

The obtaining of irradiated elastomer systems at the molecular level can be explained by the following. In systems (cis-SKB+DSCB, SKN-40+ DSCB) dispersed particles are strongly adsorbed, and then sewn to the high molecular weight fraction. The concentration of radicals in the polymer environment increases at the highest level of dose, which leads to an increase in distance between them in the consequence of which an overlap of orbits of unpaired electrons occurs in adjacent radicals [22].

On the basis of the conducted studies we can suggest the following scheme of radiation-chemical reactions of structuring of unsaturated rubbers with DSCB.

Thus, the obtained data suggest that DSCB is effective at radiolysis as a cross-linking agent (sensitizer) for unsaturated elastomers.

In conclusion, we should mention that disulfochloride aromatic compounds can be used as a sensitizer for radiation vulcanization of unsaturated elastomers (cis-SKB, SKN-26).



RH- macromolecules of rubber

4. Conclusion

In the present work we reported about conduction of radiation-chemical cross-linking of unsaturated elastomers in the presence of sensitizer agent of disulfochloride benzene. The chemical structure of macromolecules and presence of the disulfochloride benzene affects the radiation cross-linking process. Radiation cross-linking of unsaturated elastomers can be quantitatively characterized by the value of radiation-chemical yield of cross-linked molecules, effective cross-links.

Useful cross-linking sensitizers containing active halogen vigorously react with carbon molecules of unsaturated elastomer part (SKB and SKN-26). Number of soluble sol fraction is reached for both elastomers within 30-50% at doses 200kGy and after irradiation at 500kGy the polymer completely becomes insoluble. Increase in the molecular weight of elastomers during irradiation occurs with vinyl bonds located at positions of microstructure in the form of 1,2.

The output of number of cross-linked molecules ($G_{M_{nr}}$) and effective cross-links (G_{Nc}) in the system SKB + DSCB at a dose of 300kGy is $4,2 \cdot 10^5$ and $4,1 \cdot 10^5$ mol/cm³. Within the interaction of DSCB with elastomers it has been found out that there occurs a decrease in the intensity of absorption bands at 1360, 1195 and 1170cm⁻¹ characteristic for groups of -SO₂Cl. While studying the system it has been detected free radicals corresponding to EPR signal. The electrons in all studied samples in the EPR spectrum are characterized by a narrow singlet line with no trace of the hyperfine structure at cold mode 77K. There is a slight extension of lines by appearance of finely allowed spectrum of radical in the form of a narrow singlet with the width $\Delta H=1,3$ mTl and $\Delta H=1,1$ mTl. Cross-linking of elastomers are influenced by tertiary carbon atoms, linked in polybutadiene parts of the structures cis-1,2 and nitrile groups, with DSCB at dose 300kGy for the formation of cross-linking.

References

1. A. Charlesby. Atomic radiation and polymers. New York: Pergamon press, 1960. 520 p.
2. Mammadov S. M., Yadreyev F. I., Rivin E. M. Butadien-nitrilniye kauchuki i rezini na ix osnove. Baku: Elm, 1991. 280 p.

3. Makhlis F.A. Radiatsionnaya khimiya elastomerov. M.: Avtomidizdat, 1982.
4. Mammadov Sh. M.// Khim. probl. 2006, №4. pp. 648-652
5. Kuzminsky A.S., Fedoseeva T.S., Makhlis F.A. Radiatsionnaya khimiya polimerov. M.: Nauka, 1973, 292 p.
6. Mammadov S. M. Aktualniye problemi radiatsionnix issledovaniy. Baku: Elm, 1990. 260p.
7. Mammadov S. M., The Fourth Eurasian Conference on Nuclear Science and its Application. Ankara, 2007. p. 165.
8. Degtyarev E.V., Zakharov N.D.// Visokomol. Soedineniya. 1985, vol. 17, no2. p.1223
9. Pikayev A.K., Sovremennaya radiatsionnaya khimiya. Osnovniye polojeniya, eksperimentalnaya tekhnika i metodi. M.:Nauka, 1985. 289p.
10. Kuznetsov E.V., Divgun S.M., Budarina S.M. et al, Praktikum po khimii i fiziki polimerov. M.:Khimiya, 1977. 380 p.
11. Flory P., Rehner Ī. Ī.// J. Chem. Phys. 1943, №11. pp 512-520
12. Bellamy L.J. The Infrared Spectra of Complex Molecules. Chapman and Hall, 1980, v.1. 433p
13. Nelson K.B. Kolebatelniye spektri i molekularniye processi v kauchukakh: Sb. tr. VNIISK. L.: Khimiya, 1970. 150 p.
14. Bakhishev N.G. Spektroskopiya mejmolekularnikh vzaimodeystviy. L: Nauka, 1982. 305 p.
15. S.M. Mammadov, A.A. Garibov, O.H. Akperov, S.A. Rzayeva, A.K. Salehov, S.S.Ahmadova// Open J. of Phys. Chem. 2012. 2, p. 182-184 doi:10.4236/ojpc.2012.23024
16. S.M. Mammadov, S.A. Rzayeva, A.A. Garibov, O.H. Akperov, T.F. Gojayeva, J.S. Mammadov// J. of Composite Mat. 2012. 2(6). pp 137-141 doi: 10.5923/j.comaterials.20120206.04
17. Mammadov S. M.// J. Prikladnoy Khimiyi., v. 78, №9, 2005. pp. 1556-1562.
18. Mammadov S. M.// Khimiya i Neftekhimiya. 2003, №2. pp. 27-32.
19. Mammadov S. M.// J. Kauchuk i rezina. 2001, № 3. pp. 5-8.
20. Mammadov S.M., Evstigneeva R.P., Saricheva I.K., Zakharova E.P.// Khimiya Visokikh Energiy. 1991, v. 25, №5. pp. 438-442.
21. Mammadov S.M., Garibov A.A., Gasanov V.Y., Velibekova G.Z.// Khimiya Visokikh Energiy. 2010, 44, №. 4 , p. 298-301 DOI: 10.1134/S0018143910040028
22. Mammadov S.M.// Kauchuk i rezina. № 3, 2003. p. 12-15.
23. Mammadov S.M.// Azerb. Khim. Jur №1, 2005. p. 72-76.
24. Mammadov S.M. Garibov A.A., Salehov A.H.// Khimiya i Khimicheskaya Tekhnologiya. 2009, v.52, №12, p.93-99
25. Patent 205404/81 Japan: In.C: C 08
26. Patent I20090198 AZE. In.C: C 08 L 9/02 F 8/04. 2009
27. Reinholds, V. Kalkis and R.D. Maksimovs // J. Chem. Chem. Eng. 6, 2012. pp. 242-249