

Photochemical reactions in butadiene—styrene rubber

I. Influence of complex compounds of cobalt and copper on crosslinking process

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¹The influence of trace amounts of metal compounds and irradiation time on photocrosslinking process in the system butadiene—styrene copolymer with anthracene was investigated. The degree of crosslinking was evaluated according to structural changes determined by means of absorption bands in infrared and ultraviolet spectra, by determining the value of gel fraction and the limiting viscosity number of soluble portion of polymer and by analyzing the kinetic curves in the process of swelling of irradiated films. It has been found that Co(II) acetylacetonate catalyzes the crosslinking process in the whole investigated range of mass ratios (0.005—0.1 mg of catalyst for 1 g of rubber) especially in the initial stage of irradiation, while Cu(II) acetylacetonate is effective if its content is the lowest or the highest. In the presence of 0.005 mg up to 0.05 mg of Cu(II) acetylacetonate for 1 g of rubber, this substance functions partially as a catalyst of disproportionation.

¹Исследовано влияние следовых количеств металлов и продолжительности облучения на процесс фотосшивания в системе бутадиенстирольный сополимер—антрацен. Глубина сшивания оценивалась на основании структурных изменений, регистрируемых при анализе полос поглощения в ИК- и УФ-спектрах, определения величины доли гелевой формы, измерения лимитного вязкосного числа растворимой части и анализа кинетических кривых в процессе набухания облученных пленок. Было найдено, что ацетилацетонат кобальта(II) катализирует процесс сшивания во всем изучаемом диапазоне содержаний катализатора (0,005—0,1 мг катализатора на 1 г каучука), в особенности в начальной стадии облучения, в то время как ацетилацетонат меди(II) только при его самом низком или самом высоком содержаниях. При количествах от 0.005 мг/г до 0,05 мг/г каучука ацетилацетонат меди(II) частично действует как катализатор реакций диспропорционирования в полимере.

It is known that metals and metal compounds even in trace amounts may significantly affect the process of formation and destruction of high-molecular substances. The effect of these compounds in thermo- and photodegradation processes of polymers is dependent on structure of the used polymer as well as on character of the central atom and ligand in the complex compound. Moreover, it depends on its amount, temperature, and wavelength of radiation.

The metals of variable valence (Cu, Co, Ni, Cr, Fe, Mn) are able to split homolytically peroxy compounds in the course of thermooxidation as well as to support the formation of radicals and peroxy compounds. Besides acceleration of the initiation stage of radical-chain process, the rate of propagation and termination reactions is also influenced. *Kuzminskii* [1] and *Cooper* with co-workers [2] have found that the influence of metal complex compounds on the acceleration of the chain thermooxidation process is dependent on the character of the bond between central atom and ligand as well as on their structure.

Much attention was paid to the effect of metals and metal compounds on the photooxidative destruction of polymers [3—7]. The results of these studies are not consistent and different views and conclusions result from comparisons of the course of thermo- and photooxidative processes in the investigated polymer. *Takahashi et al.* [3] and *Charlesby* [4] have found a comparable catalytic effect of metal compounds in photo- and thermooxidation of polymer substances whereas *Osawa et al.* [5, 6, 8] have observed the effect of opposite character. The authors mentioned before allege that the influence of some metal compounds on photooxidation and thermooxidation may be contrary in the absence of polymer carbonyl groups. Furthermore, they have observed that a change in the amount of metal compounds in the substrate may result in the fact that their function in the course of photodegradation loses the accelerating character and starts to have retardation effect. According to the authors, the retardation effect of some metal compounds is to be explained by their several possible functions. They assume that these compounds can decompose hydroperoxides in nonradical way or function as UV absorbers or acceptors of energy of excited polymeric structures (quenchers of triplet states). *Ranaweera and Scott* [9—11] studied the quenching ability of some Ni, Fe, and Cu complex compounds in ultraviolet photostabilization of polymers. They have found that the UV stabilizing activity of metal complex may be due to its UV shielding effect or to its ability to decompose in nonradical way hydroperoxides to nonreactive products and thus manifest their autosynergic-inhibitory mechanism.

The catalytic effect of acetylacetonates is caused by their decomposition into radical fragments with relatively high quantum yields owing to irradiation by ultraviolet radiation and so they can in further stage initiate the decomposition of peroxides and hydroperoxides [12].

Čeppan et al. [13] have theoretically proved the photoinitiated formation of

dioxyanthracene catalyzed by metals of variable valence which can in further split into reactive oxygen radicals able to branch and crosslink the irradiated polymer.

In this paper, we have studied the influence of the amount of metal compounds $\text{Co}(\text{acac})_2$ and $\text{Cu}(\text{acac})_2$ as well as of irradiation time on the photocrosslinking process of butadiene—styrene copolymer in the presence of constant content of anthracene functioning as a crosslinking initiator.

Experimental

The investigated butadiene—styrene copolymer (commercial name Kralex 010.401) was produced by cold emulsion polymerization in the presence of 1—2 mass % of a dying stabilizer which was not further identified. The copolymer was not treated for kinetic measurements. The course of photochemical reactions was investigated in the presence of constant quantity of crosslinking initiator, *i.e.* anthracene of anal. grade (Lachema, Brno) and varying quantity of metal compounds of variable valence in the form of $\text{M}(\text{acac})_2$. $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ acetylacetonates were synthesized from anal. grade chemicals and recrystallized several times in methanol. Before use, they were activated at 90 °C in slight vacuum up to colour change to remove water. The copolymer subjected to photooxidation was in the form of film the width of which was 2.3×10^{-3} cm— 2.5×10^{-3} cm. The kinetic measurements were carried out in an interrupted test [14]. The preparation of films and the control of their widths were described earlier [14]. The solutions for casting the films contained 1 g of rubber, 0.01 g of anthracene, the investigated quantity of metal compounds, and 25 cm³ of anal. grade chloroform.

The source of radiation was a high-pressure mercury lamp 500 W, HBO 500 (Narva, BGW, Berlin, GDR) with a protecting jacket. The distance of samples from the source of radiation was 8.5 cm.

The content of gel fraction was determined by standard filtration procedure after benzene extraction.

The viscosity of the product obtained from filtrate was measured with a viscosimeter with hanging level adapted to diluting of the solutions at constant temperature (25.0 ± 0.1) °C. Anal. grade benzene was used as a solvent. The limiting viscosity numbers $[\eta]$ were determined from the measured values of viscosity for individual times of irradiation by extrapolation for zero concentration.

The kinetics of swelling of rubber films on NaCl plates after irradiation was investigated by the Dogadkin method [15]. The film widths were equal to those ones used for spectroscopic measurements.

The infrared absorption spectra were taken with a registration Perkin—Elmer spectrometer (Infrared Spectrometer 599) with the wavenumber range 4000—200 cm⁻¹ and resolving power 0.1—0.02 cm⁻¹.

The electronic absorption spectra in the ultraviolet region were measured with a registration spectrophotometer Specord (Zeiss, Jena) with the wavelength range 200—800 nm and accuracy of measurement $\pm 0.2\%$.

Results and discussion

The structural changes produced by irradiation of the investigated copolymer in the presence of constant quantity of complex compounds were evaluated:

1. according to temporal change of characteristic absorption bands in the infrared spectral region ($\tilde{\nu}/\text{cm}^{-1} = 3400, 1731, 1699, 970, \text{ and } 920$) as well as in the ultraviolet spectral region ($\lambda = 382 \text{ nm}$). The values of ΔA on kinetic curves give the change in absorbance at a given wavelength during irradiation with respect to the nonirradiated film;

2. by determining the quantity of crosslinked polymer (gel fraction);

3. by determining the limiting viscosity numbers $[\eta]$ of the soluble portion of polymer;

4. according to the maximum amount of the liquid Q_m penetrated in the irradiated swelling polymer.

1. The change in absorbance of the band ΔA at $\tilde{\nu} = 3400 \text{ cm}^{-1}$ characteristic for vibrations of the $-\text{OH}$ groups after 15 min and 60 min irradiation for Krallex

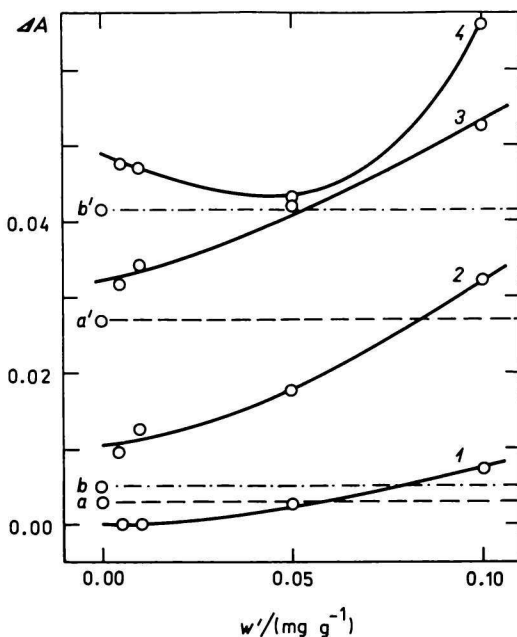


Fig. 1. Dependence of the change in absorbance ΔA of the band at $\tilde{\nu} = 3400 \text{ cm}^{-1}$ on quantity of the added metal compounds for individual times of irradiation.

1. $\text{Co}(\text{acac})_2$, $t = 15 \text{ min}$; 2. $\text{Cu}(\text{acac})_2$, $t = 15 \text{ min}$; 3. $\text{Co}(\text{acac})_2$, $t = 60 \text{ min}$; 4. $\text{Cu}(\text{acac})_2$, $t = 60 \text{ min}$.
 a) Without admixtures, $t = 15 \text{ min}$; b) rubber + anthracene, $t = 15 \text{ min}$; a') without admixtures, $t = 60 \text{ min}$; b') rubber + anthracene, $t = 60 \text{ min}$.

010.401 with an addition of 1 mass % of anthracene and individual metal compounds in the amounts of 0.005—0.1 mg for 1 g of rubber is represented in Fig. 1. After 60 min irradiation, the dependence exhibits a minimum at the content 0.05 mg of Cu(II) chelate to 1 g of rubber, while it has increasing tendency in the whole investigated interval of mass ratios for both times of irradiation in the presence of Co(acac)₂. As obvious from the curves, the influence of increasing amount of Cu(acac)₂ on the formation of the —OH groups is greater than that of Co(acac)₂.

The formation of carbonyl oxidation products caused by the effect of different quantities of individual metal compounds and by different times of irradiation was investigated on the basis of the change in absorbance of the band at $\tilde{\nu} = 1731 \text{ cm}^{-1}$ (Fig. 2) which corresponded to saturated aldehydes and of the band at $\tilde{\nu} = 1699 \text{ cm}^{-1}$ (Fig. 3) which corresponded to unsaturated aldehydes. The curves in Fig. 2 show that Co(acac)₂ has a greater catalytic effect on the formation of saturated aldehydes only from the mass ratio 0.05 mg for 1 g of rubber in comparison to Cu(acac)₂. On the other hand, curve 2 in Fig. 3 corresponding to $\Delta A(\text{C}=\text{O})$ at $\tilde{\nu} = 1699 \text{ cm}^{-1}$ for Cu(acac)₂ after 15 min irradiation at the investigated mass ratios exhibits a minimum, while curve 1 for Co(acac)₂ has slightly rising tendency under equal conditions. The observed falls of $\Delta A(\text{C}=\text{O})$ for both

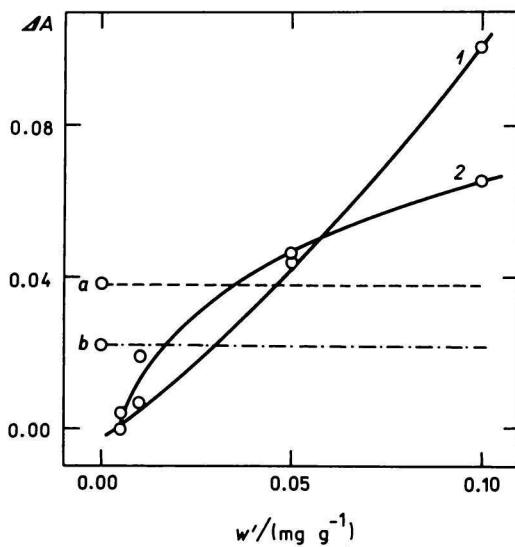


Fig. 2. Dependence of the change in absorbance ΔA of the band at $\tilde{\nu} = 1731 \text{ cm}^{-1}$ on quantity of the added metal compounds after irradiation time of 15 min.

1. Co(acac)₂; 2. Cu(acac)₂.

a) Without admixtures; b) rubber + anthracene.

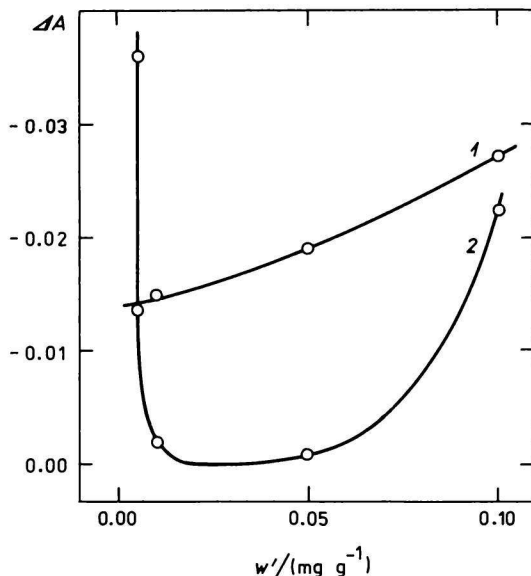


Fig. 3. Dependence of the change in absorbance ΔA of the band at $\tilde{\nu} = 1699 \text{ cm}^{-1}$ on quantity of the added metal admixtures after 15 min irradiation.

1. $\text{Co}(\text{acac})_2$; 2. $\text{Cu}(\text{acac})_2$.

metal compounds in the whole investigated interval of mass ratios are, however, considerably smaller than observed for polymer without admixtures, where $\Delta A(\text{C}=\text{O}) = -0.105$ as well as for irradiated polymer with the addition of 1 mass % of anthracene, where $\Delta A(\text{C}=\text{O}) = -0.08$, so the result is that the presence of metal compounds in the system has not significant influence on the change in content of unsaturated aldehydes or retards their formation.

The change in unsaturation of the chain during irradiation was investigated by measuring the absorbance of the bands at $\tilde{\nu} = 970 \text{ cm}^{-1}$ and $\tilde{\nu} = 920 \text{ cm}^{-1}$ which correspond to vibrations of the $-\text{CH}=\text{CH}-$ groups in the 1—4 *cis* and 1—4 *trans* butadiene polymeric units. It was observed that the absorbance of the investigated bands visibly decreased with irradiation time. The curves expressing the dependence of the change in absorbance of the above-mentioned two bands on amount of the added $\text{Co}(\text{acac})_2$ for a constant irradiation time (15 min) exhibit opposite courses (Fig. 4). The influence of the presence of $\text{Cu}(\text{acac})_2$ on the change in absorbance of the mentioned bands was not observed.

As for the ultraviolet spectrum, the greatest change in the course of irradiation was observed in the absorption bands at $\lambda = 382 \text{ nm}$ which corresponded to unsaturated double bonds in the polymer chain. This absorption band was, however, measured in the absence of metal compounds, too. The character of

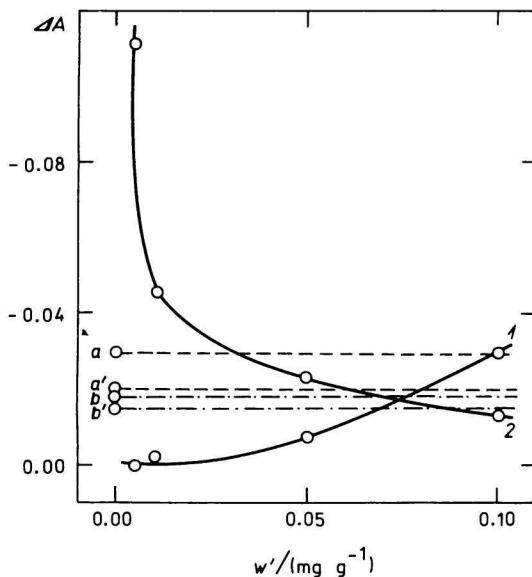


Fig. 4. Dependence of the change in absorbance ΔA of the bands at $\tilde{\nu} = 920 \text{ cm}^{-1}$ and $\tilde{\nu} = 970 \text{ cm}^{-1}$ on quantity of the added $\text{Co}(\text{acac})_2$ after 15 min irradiation.

1. $\tilde{\nu} = 970 \text{ cm}^{-1}$; 2. $\tilde{\nu} = 920 \text{ cm}^{-1}$

a) Without admixtures ($\tilde{\nu} = 920 \text{ cm}^{-1}$); b) rubber + anthracene ($\tilde{\nu} = 920 \text{ cm}^{-1}$); a') without admixtures ($\tilde{\nu} = 970 \text{ cm}^{-1}$); b') rubber + anthracene ($\tilde{\nu} = 970 \text{ cm}^{-1}$).

curves indicates a loss in unsaturation of these chains, especially in initial stage of photooxidation process. It appears from the investigated mass ratios of metal compound to rubber after 15 min and 60 min irradiation (Fig. 5) that $\text{Co}(\text{acac})_2$ has a more significant effect on the loss in unsaturation than $\text{Cu}(\text{acac})_2$. It is very likely that $\text{Cu}(\text{acac})_2$ loses its catalytic activity in the ultraviolet region by absorbance of radiation owing to which it is partially effective as an ultraviolet screen [5].

2. The course of photocrosslinking reactions was investigated by determining the quantity of crosslinked polymer, *i.e.* the gel fraction W (mass %) depending on the time of irradiation at a constant addition of $\text{Cu}(\text{acac})_2$ and the amounts of the acetylacetonates added for individual irradiation times. The quantity of gel fraction as a function of varying content of the investigated metal compounds after 2 min, 15 min, 30 min, and 60 min irradiation is represented in Figs. 6 and 7. It is obvious that the quantity of gel fraction in polymer increases with irradiation time for all investigated mass ratios of acetylacetonate to rubber. The plots found for $\text{Cu}(\text{acac})_2$ and all investigated time intervals of irradiation exhibit a minimum at 0.05 mg of compound for 1 g of rubber, which is most obvious after the time of irradiation of

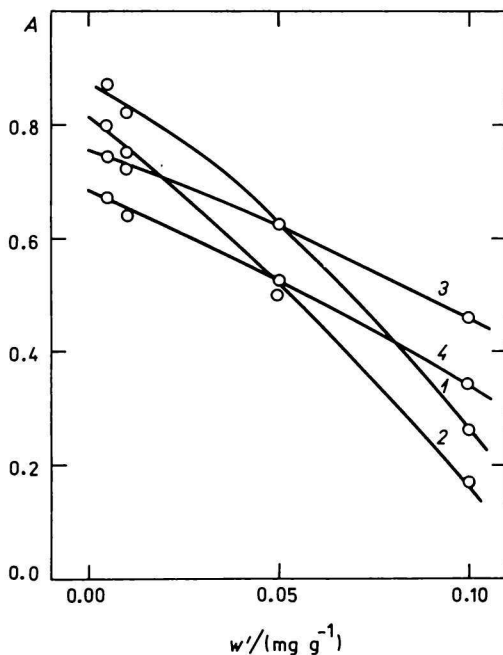


Fig. 5. Dependence of absorbance A of the band at $\lambda = 382$ nm on quantity of the added metal compounds for individual times of irradiation.

1. $\text{Co}(\text{acac})_2$, $t = 15$ min; 2. $\text{Co}(\text{acac})_2$, $t = 60$ min;
3. $\text{Cu}(\text{acac})_2$, $t = 15$ min; 4. $\text{Cu}(\text{acac})_2$, $t = 60$ min.

2 min (Fig. 7). This minimum gradually disappears with extension of irradiation time (over 15 min), but the content of gel fraction still increases. In the first approximation, we may state that $\text{Cu}(\text{acac})_2$ up to the limit of 0.05 mg per 1 g of rubber favours the disproportionation reactions with respect to crosslinking reactions, which manifests itself by a decrease in content of the gel fraction.

The quantity of gel fraction increases with the amount of the added $\text{Co}(\text{acac})_2$ (Fig. 6) and the greatest change in its value is to be observed for the irradiation time between 2 min and 15 min. The rising trend of curves according to addition of $\text{Co}(\text{acac})_2$ vanishes with extension of radiation exposure and the gel fraction for the investigated mass ratio of $\text{Co}(\text{acac})_2$ to rubber remains constant. We may state that, in contrast to $\text{Cu}(\text{acac})_2$, a higher content of $\text{Co}(\text{acac})_2$ (over 0.05 mg/1 g rubber) does not affect more significantly the process of crosslinking.

Though the dependence of the content of gel fraction on the quantity of the added $\text{Cu}(\text{acac})_2$ exhibits a minimum in the whole investigated time interval of irradiation, the absolute values of gel fraction are higher in comparison with the values found for a system in which $\text{Co}(\text{acac})_2$ is present.

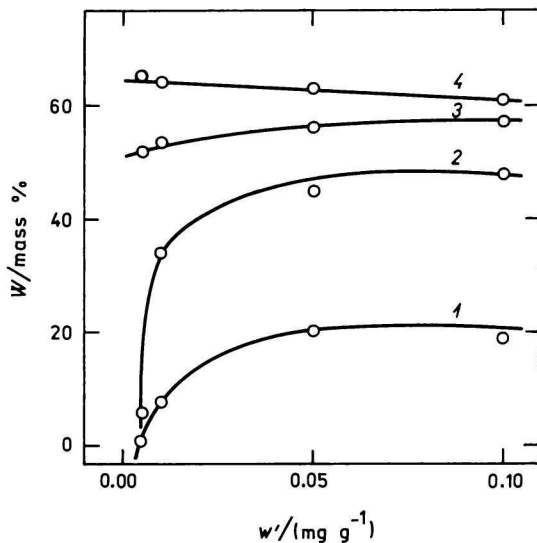


Fig. 6. Change in gel fraction ($W/\text{mass } \%$) as a function of quantity of the added $\text{Co}(\text{acac})_2$ for individual times of irradiation.

1. $t = 2$ min; 2. $t = 15$ min; 3. $t = 30$ min; 4. $t = 60$ min.

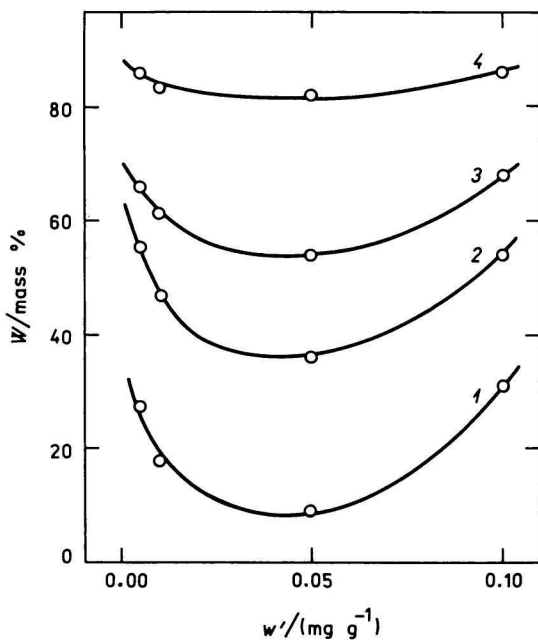


Fig. 7. Change in gel fraction ($W/\text{mass } \%$) as a function of quantity of the added $\text{Cu}(\text{acac})_2$ for individual times of irradiation.

1. $t = 2$ min; 2. $t = 15$ min; 3. $t = 30$ min; 4. $t = 60$ min.

3. The soluble portion of polymer after irradiation for different times in the presence of variable amounts of complex metal compounds was characterized by the change in limiting viscosity number $[\eta]$. The dependences of $[\eta]$ on quantity of the added acetylacetonates for individual times of irradiation are represented in Figs. 8 and 9. The course of the curves in Fig. 8 shows an evident decrease in limiting viscosity number for the samples containing $\text{Co}(\text{acac})_2$ up to exposure of 15 min. The mean molar mass of polymer decreases with decreasing $[\eta]$, which indicates that the bonds of polymer chain are initially broken at short irradiation times and it may be assumed that longer chains preferentially participate in crosslinking and branching.

As for $\text{Cu}(\text{acac})_2$ (Fig. 9), the dependence on quantity of the added metal compounds exhibits a maximum which is the most obvious after irradiation time of 2 min. This plot becomes linear after 30 min exposure. It may be assumed that $\text{Cu}(\text{acac})_2$ effectively catalyzes in the first stage of irradiation the reactions which bring about the growth of polymer chains in the soluble phase or the segments of lower molecular mass also take part in crosslinking and branching.

4. The influence of admixtures of metal compounds on photocrosslinking process of the investigated copolymer was also valuated on the basis of the change in maximum volume of the absorbed low-molecular penetrant, *i.e.* benzene (Q_{max})

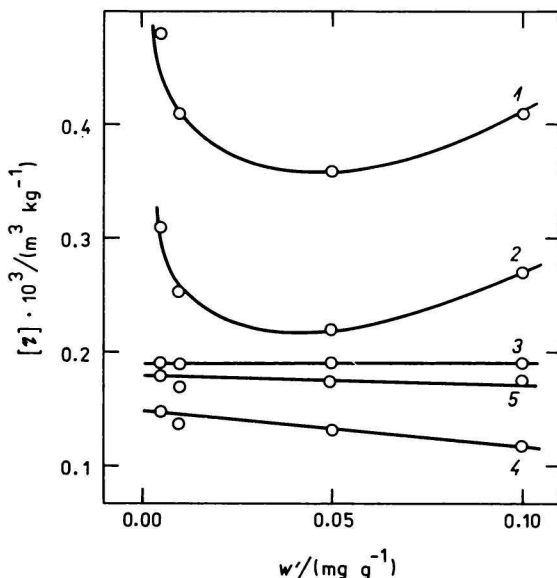


Fig. 8. Dependence of limiting viscosity number $[\eta]$ on quantity of the added $\text{Co}(\text{acac})_2$ for individual times of irradiation.

1. $t = 2$ min; 2. $t = 8$ min; 3. $t = 15$ min; 4. $t = 30$ min; 5. $t = 60$ min.

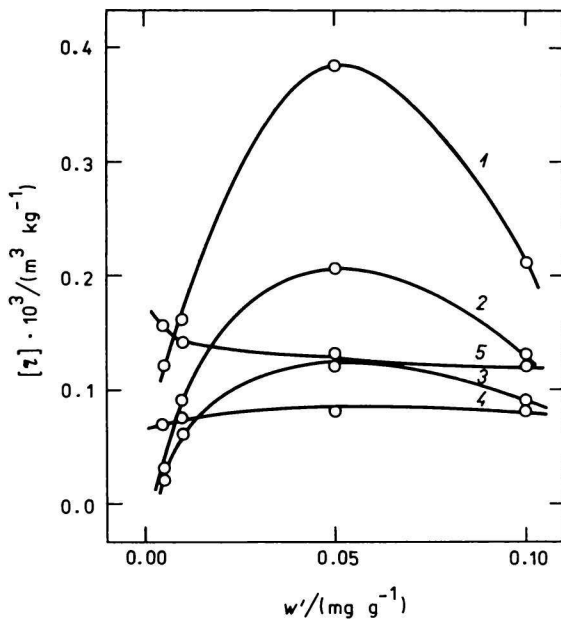


Fig. 9. Dependence of limiting viscosity number $[\eta]$ on quantity of the added $\text{Cu}(\text{acac})_2$ for individual times of irradiation.

1. $t = 2$ min; 2. $t = 8$ min; 3. $t = 15$ min; 4. $t = 30$ min; 5. $t = 60$ min.

which was determined from kinetic curves of the swelling of films (Fig. 10) depending on irradiation time for constant quantities of acetylacetonates and on quantities of the added metal complexes for individual irradiation times (Table 1). It is evident that the greatest change in the values of Q_{\max} appeared for both metal

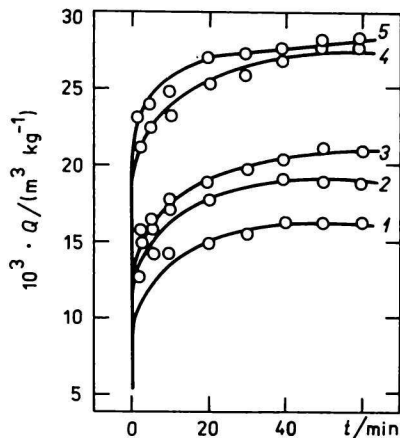


Fig. 10. Volume of the absorbed penetrant Q as a function of swelling time in irradiated rubber films containing $0.1 \text{ mg Co}(\text{acac})_2/1 \text{ g}$ rubber.

1. $t = 2$ min; 2. $t = 8$ min; 3. $t = 15$ min;
4. $t = 30$ min; 5. $t = 60$ min.

Table 1

Influence of admixtures of metal compounds on photocrosslinking process of the investigated copolymer

$\frac{w'}{\text{mg/g rubber}}$	Irradiation time min	Co(acac) ₂				Cu(acac) ₂		
		$\frac{W}{\text{mass \%}}$	$\frac{10^3 \cdot Q_{\text{max}}}{\text{cm}^3 \text{ g}^{-1}}$	$\frac{W/Q_{\text{max}}}{\text{mass \% g cm}^{-3}}$	$\frac{10^{11} \bar{D}_{\text{bcnr}}}{\text{m}^2 \text{ s}^{-1}}$	$\frac{W}{\text{mass \%}}$	$\frac{10^3 \cdot Q_{\text{max}}}{\text{cm}^3 \text{ g}^{-1}}$	$\frac{W/Q_{\text{max}}}{\text{mass \% g cm}^{-3}}$
0.005	2	1	18	0.06	2.47	28	18	1.55
	15	6	28	0.21	0.49	54	26	2.08
	30	51	33.5	1.52	—	67	27.5	2.43
	60	64	36	1.78	—	86	29	2.96
0.01	2	12	17.5	0.12	2.18	15	19	0.79
	15	41	25.5	1.61	0.33	42	26	1.62
	30	58	30	1.93	—	58	28.5	2.04
	60	63.5	33.5	1.89	—	81	30	2.70
0.05	2	18	16.5	1.09	—	9	20	0.45
	15	48	23.5	2.04	—	36	26	1.38
	30	58	28	2.07	—	55	29	1.89
	60	62	31	2.00	—	82	32	2.56
0.1	2	20.5	16	1.28	—	31	21	1.48
	15	49	21	2.34	—	55	26	2.12
	30	58	25	2.32	—	68	30	2.27
	60	61	29	2.10	—	86	33	2.62

compounds up to irradiation times below 15 min, while an increasing content of metal chelates had no significant influence on this change.

The dependence of the ratio of gel fraction (W) to maximum amount of the absorbed low-molecular penetrant in an irradiated polymeric matrix (Q_{\max}) on irradiation time for different contents of individual metal compounds (Figs. 11 and 12) indicates a different course of crosslinking reactions in the presence of $\text{Co}(\text{acac})_2$ and $\text{Cu}(\text{acac})_2$. As for $\text{Co}(\text{acac})_2$ (Fig. 11), the most efficient crosslinking and branching takes place in the first stage of irradiation and the ratio W/Q_{\max} increases with the content of chelate, too. For $\text{Cu}(\text{acac})_2$ (Fig. 12), the ratio W/Q_{\max} exponentially rises with irradiation time for each mass ratio. This ratio at equal irradiation time decreases with increasing content of copper chelate up to 0.05 mg/1 g rubber and further it increases almost to the values corresponding to the lowest content of chelate at the content 0.1 g $\text{Cu}(\text{acac})_2$ /1 g rubber. These relationships are in agreement with the results represented in Figs. 6 and 7.

The decrease in the mean integral diffusion coefficients \bar{D} of benzene determined from kinetic curves of swelling [16] (Table 1) which is due to increasing time of irradiation and increasing content of metal compounds for the samples with

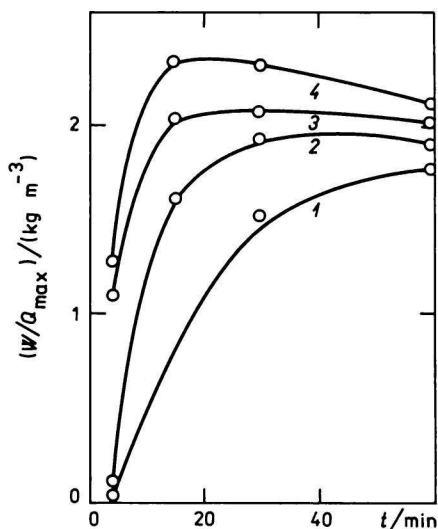


Fig. 11. Dependence of W/Q_{\max} on irradiation time for individual mass ratios ($m(\text{Co}(\text{acac})_2)/m(\text{rubber})$)/(mg g^{-1}).
1. 0.005; 2. 0.01; 3. 0.05; 4. 0.1.

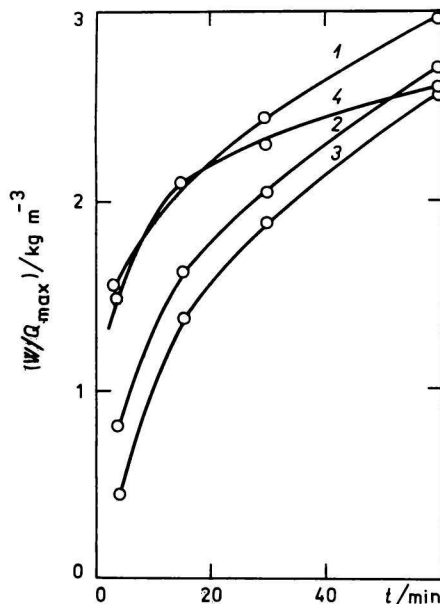


Fig. 12. Dependence of W/Q_{\max} on irradiation time for individual mass ratios ($m(\text{Cu}(\text{acac})_2)/m(\text{rubber})$)/(mg g^{-1}).
1. 0.005; 2. 0.01; 3. 0.05; 4. 0.1.

$\text{Co}(\text{acac})_2$ indicates the initiating influence of metal complex in the crosslinking process. The values of the mean integral diffusion coefficients were determined on the basis of the model put forward for the calculation of \bar{D} in the solid phase [17—19].

It results from the data obtained by investigating the temporal changes of the characteristic absorption bands produced by irradiation in the infrared and ultraviolet spectral region that the influence of the investigated $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ acetylacetonates (0.005 mg—0.1 mg for 1 g of rubber) on absorbance of some bands is not negligible.

As for $\text{Co}(\text{acac})_2$, its increasing content in the system manifests itself in photochemical reactions — oxidation, branching, crosslinking, and degradation — up to irradiation time 15 min. After this time interval, the investigated properties of the system practically remain without change.

After addition of $\text{Cu}(\text{acac})_2$ in the mass ratio range 0.005—0.05 mg for 1 g of rubber, the content of crosslinked structures probably decreases for all irradiation times, which may be due to disproportionation reactions. The course of reactions especially in the crosslinking process at mass ratio 0.1 mg/1 g rubber is analogous to that observed in the presence of $\text{Co}(\text{acac})_2$.

We cannot unambiguously correlate the values of Q_{max} with the values of gel fraction W because a change in polarity of the substrate is possible or, because of the presence of anthracene, a sensitized branching process involving an increase in side polymer chains as well as chains with the bonded anthracene molecules or its fragments may appear in the course of photochemical processes in the investigated multicomponent system. The branched macromolecular chains exhibit lower viscosity and greater ability of detaining the penetrant (benzene) in the process of swelling.

In agreement with literature data, a greater catalytic activity of $\text{Cu}(\text{acac})_2$ with respect to photooxidation, observed according to changes in the infrared and ultraviolet spectral regions was confirmed. An exception to this observation consists in the fact that the formation of saturated aldehydic oxidation products is more intensively catalyzed by $\text{Co}(\text{acac})_2$.

The observed decrease in limiting viscosity number $[\eta]$ and relative molecular mass M_w of the soluble portion with irradiation time is consistent with literature data [20].

A more detailed explanation based on experimental investigation of all possible reactions in a so complicated system will require further studies irrespective of the fact that the photochemical reactions of fundamental components are known and described in literature.

References

1. Kuzminskii, A. S., *Starenie i stabilizatsiya polimerov*, p. 291. Nauka, Moscow, 1964.
2. Cooper, T. A., Clifford, A. A., Mills, D. J., and Waters, W. A., *J. Chem. Soc. B*1966, 793.
3. Takahashi, T. and Suzuki, K., *Kobunshi Kagaku (Polym. Chem.) (Japan)* 21, 487, 494, 498 (1964).
4. Charlesby, A. and Partridge, R. H., *Proc. Roy. Soc. (London)* 283A, 312, 329 (1965).
5. Osawa, Z., Kurisu, N., Nagashima, K., and Nakano, K., *J. Appl. Polym. Sci.* 23, 3583 (1979).
6. Osawa, Z. and Nakano, K., *J. Polym. Sci., Symp. No. 57*, 267 (1976).
7. Laver, H. S., *Developments in Polymer Stabilization*, Vol. 1. (Scott, G., Editor.) Appl. Sci. Publ., Essex, 1980.
8. Osawa, Z., Shibamiya, T., and Matsuzaki, K., *Kogyo Kagaku Zasshi* 71, 552 (1968).
9. Ranaweera, R. P. R. and Scott, G., *Chem. Ind. (London)* 1974, 774.
10. Ranaweera, R. P. R. and Scott, G., *J. Polym. Sci., Polym. Lett. Ed.* 13, 71 (1975).
11. Ranaweera, R. P. R. and Scott, G., *Eur. Polym. J.* 12, 591, 825 (1976).
12. Lintvedt, R. L., *Concepts of Inorganic Photochemistry*. (Adamson, A. W. and Fleischauer, P. D., Editors.) Wiley, New York, 1975.
13. Čeppan, M., Lapčík, L., Liška, M., and Pelikán, P., *Eur. Polym. J.* 16, 607 (1980).
14. Kellö, V. and Tkáč, A., *Chem. Zvesti* 7, 129 (1953).
15. Ulický, L. and Vavra, J., *Fyzikálna chémia — Laboratórne cvičenia*. (Physical Chemistry — Laboratory Exercises.) P. 219. Alfa Publishers, Bratislava, 1974.
16. Crans, J., *The Mathematics of Diffusion*, Chapter 11. Oxford University Press, Oxford, 1956.
17. Wilkens, J. B. and Long, F. A., *Trans. Faraday Soc.* 53, 1146 (1957).
18. Meares, P., *J. Polym. Sci.* 27, 391 (1958).
19. Fujita, H., Kishimoto, A., and Matsumoto, K., *Trans. Faraday Soc.* 56, 424 (1960).
20. Rånby, B. and Rabek, J. F., *Photodegradation, Photooxidation and Photostabilization of Polymers*, p. 94. (Russian translation.) Mir, Moscow, 1978.

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