

**Photocross-linking process in butadiene-styrene rubber
in the presence of anthracene
Influence of dimethyldithiocarbamates of metals
of variable valence**

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The influence of trace amounts of dimethyldithiocarbamates of metals of variable valence (Ni(II), Co(II), Cu(II), and Fe(III)) and of time of irradiation with polychromatic ultraviolet light on cross-linking process in the system butadiene-styrene rubber—anthracene has been studied. As to the degree of cross-linking, conclusions were drawn from the amount of the insoluble polymer fraction after irradiation. The photocross-linking process in polymer was investigated on the basis of change in absorbance of some characteristic bands of atomic groups in infrared and ultraviolet spectral region. It has been found that all investigated complex compounds catalyze the photocross-linking process in the copolymer. The rate and efficiency of cross-linking is predominantly determined by the central metal atom and that is why the course of the structural changes in substrate due to irradiation is differently influenced by the investigated individual metal complex compounds with equal ligand.

Исследовалось влияние следовых количеств диметилдителиокарбаматов металлов переменной валентности (Ni(II), Co(II), Cu(II) и Fe(III)), а также продолжительности облучения полихроматическим УФ-светом на процесс сшивания в системе бутадиев-стирольный каучук—антрацен. О степени сшитости делался вывод на основе количества нерастворимой доли полимера после облучения. Процесс фотосшивания в полимере наблюдался на основе изменения поглощения некоторых характеристических полос атомных групп в ИК- и УФ-областях спектра. Обнаружено, что все исследуемые комплексные соединения катализируют процесс фотосшивания в сополимере. Скорость и эффективность сшивания определяются преимущественно

центральным атомом металла, и, поэтому, на протекание структурных изменений в субстрате под действием облучения по разному влияли комплексные соединения различных металлов с одинаковым лигандом.

It is known from literature that the presence of metal complex compounds significantly affects the photocross-linking process in polymers [1—4]. Even for very simple metal complexes of variable valence we are not able to fully recognize the function of ligands and that of the central metal atom. The ligands can immediately participate in reactions by forming weak bonds with near groups as well as with remote groups by far range interaction which controls the orientation of other ligands and circumscribes the number of parts able to enter into coordination. The ligands can also affect the oxidation degree of the metal atom and its electronegativity and polarizability. The catalytic activity of the central atom may also be indirectly influenced *e.g.* by the stabilization of ligands caused by origination of the π -bonds with other ligands or by the *cis* and *trans* configuration of ligands. Besides the mentioned factors, the catalytic efficiency of the complex compound also depends on the space arrangement of substrate. It may be assumed that any metal with variable valence bonded to appropriate ligands ought to catalyze the type of reaction in the required line in a given system.

It has been revealed by investigating the influence of ligand of metal compounds that trace amounts of nickel dimethyldithiocarbamate ($\text{Ni}(\text{DMDTC})_2$) exhibit higher catalytic activity in the cross-linking process of butadiene-styrene (BS) rubber than nickel acetylacetonate ($\text{Ni}(\text{acac})_2$) and nickel diisopropylsalicylate ($\text{Ni}(\text{DIPS})_2$) [5]. The complexes of Fe(II) and Fe(III) are also frequently used as compounds influencing the photoprocesses in polymers. It has been disclosed that $\text{Fe}(\text{acac})_3$ is an efficient photodegradation initiator for polyethylene [6] and small amounts of iron(III) stearates accelerate the generation of radicals in irradiated polyethylene samples [7, 8]. *Scott* and coworkers [9—11] revealed a lower photostability of the Fe(III) complexes when compared with the Ni(II), Co(II), and Cu(II) complexes and confirmed the activating effect of Fe(III) dithiocarbamate in the course of photooxidation of polymers. The authors assume that a low light stability brings about a photoreduction of the Fe(III) complex to Fe(II) complex and generation of the dithiocarbamoyl radical functioning as a photoinitiator.

In this study we examined the influence of the Co(II), Cu(II), Ni(II), and Fe(III) dimethyldithiocarbamates on the course of photocross-linking process of the BS rubber Kralex 010.401 (without treatment) in the presence of constant anthracene amount (1 mass %) working as cross-linking agents. We investigated the influence of irradiation time of samples using ultraviolet light and of varying

amounts of the added complex compounds on the photocross-linking process in the studied system by determining the insoluble polymer fraction and by measuring the changes in absorbance of individual bands in the infrared and ultraviolet spectral regions before and after irradiation.

Experimental

The solutions used for films casting were prepared by dissolving 1 g of BS rubber, 0.01 g of anthracene and the fixed amount of complex compound in 30 cm³ of chloroform. The amounts of dimethyldithiocarbamates added into rubber were (w) 5, 10, 50, and 100 ppm. The individual samples of DMDTC were prepared in the Department of Physical Chemistry and their purity was checked by determining the melting point. The determined purity was satisfactory for EPR spectroscopic measurements. Other chemicals used were anal. grade reagents. The films were prepared by casting the solutions on NaCl plates. The width of films was checked by measuring absorbance of the band at $\tilde{\nu} = 1458 \text{ cm}^{-1}$ (bending vibration of the C—H bonds in CH₂ and CH₃) and varied in the interval $\lambda = 0.023\text{—}0.026 \text{ nm}$. The films were irradiated in air at laboratory temperature for 0, 3, 7, 15, 30, and 60 min by the use of a high-pressure mercury discharge tube 500 W (HBO 500) with polychromatic radiation placed in a protecting jacket. The range of wavelengths was 300—600 nm and the maximum intensity occurred at the wavelengths of 360 and 440 nm. The distance of samples from the tube was 8.5 cm.

The quantity of the gel fraction determined gravimetrically was expressed in relation to the mass of film $w(\text{gel}) = m(\text{gel})/m(\text{film})$. The maximal deviation of determined $w(\text{gel})$ was ± 0.015 .

The infrared absorption spectra were recorded on an instrument Perkin—Elmer, model 554 and the electronic absorption spectra were taken with a Specord UV VIS spectrophotometer.

Results and discussion

Similarly as found by studying the influence of different ligands, bound to equal central metal atom [5], on the photocross-linking process in rubber, the examination of the influence of equal ligand, *i.e.* DMDTC bonded to different metals of variable valence has shown that the content of gel fraction in butadiene-styrene rubber increases with exposure time.

The content of gel fraction found for increasing additions of metal dimethyldithiocarbamates at particular constant irradiation times (Figs. 1—4) indicates different catalytic activity of individual metal complexes with respect to the photocross-linking process in the investigated system.

As to addition of Ni(DMDTC)₂, the quantity of gel fraction does not change with increasing content of the complex up to 15 min of irradiation. Afterwards,

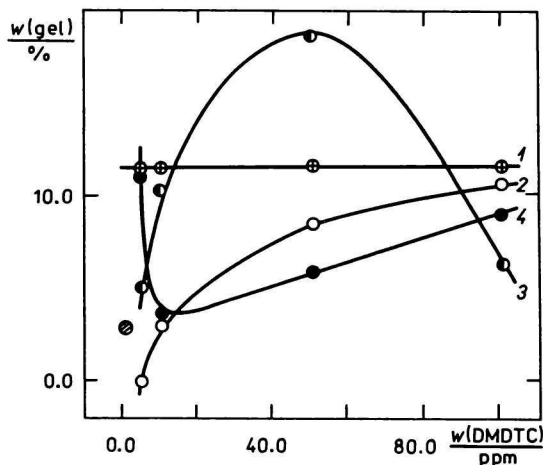


Fig. 1. Variation of the content of gel fraction w with amount of the added metal dimethyldithiocarbamate for constant irradiation time of BS films (3 min). 1. Ni(II); 2. Co(II); 3. Cu(II); 4. Fe(III); \otimes — BS rubber irradiated without any addition of metal complex.

the curves expressing this relation exhibit an upgrade trend. Whatever addition of $\text{Co}(\text{DMDTC})_2$ raises the content of gel fraction at every prolonged irradiation time. The graphs describing the dependence of the gel fraction w on

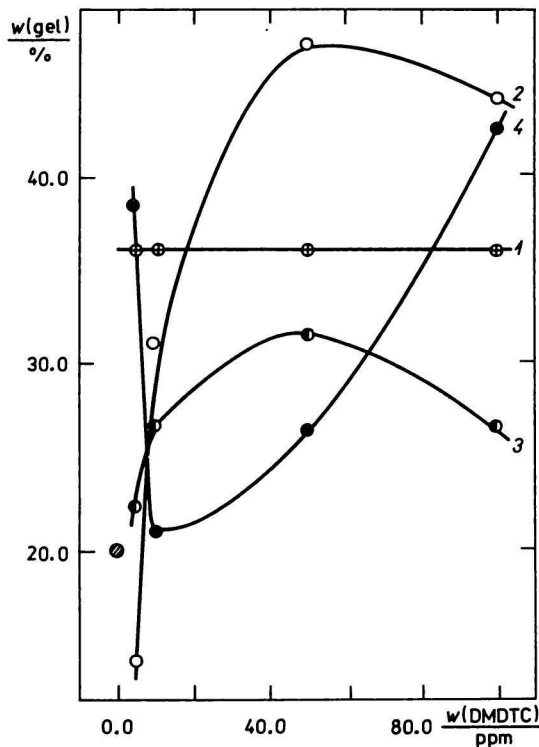
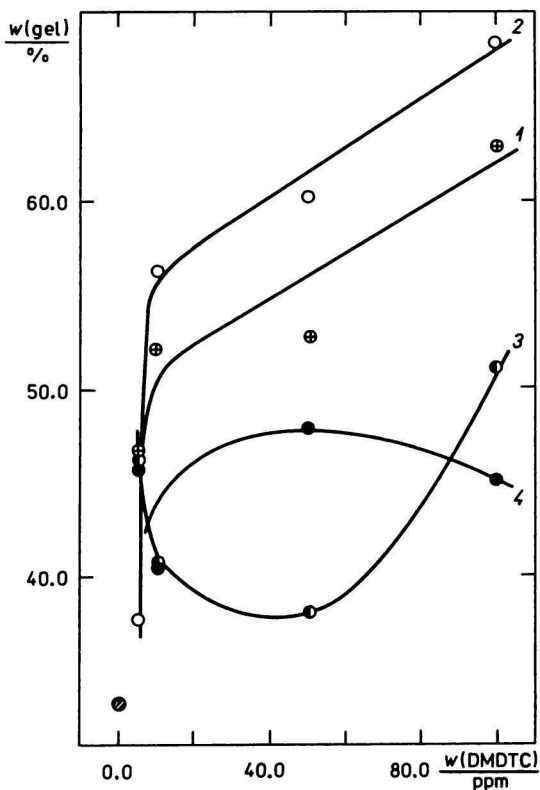


Fig. 2. Variation of the content of gel fraction w with amount of the added metal dimethyldithiocarbamate for constant irradiation time of BS films (15 min). The denotation is the same as in Fig. 1.

Fig. 3. Variation of the content of gel fraction w with amount of the added metal dimethyldithiocarbamate for constant irradiation time of BS films (30 min). The denotation is the same as in Fig. 1.



quantity of the added $\text{Cu}(\text{DMDTC})_2$ exhibit a maximum at about $w = 50$ ppm for every irradiation time. The presence of $\text{Fe}(\text{DMDTC})_3$ up to 10 ppm results in a decrease in quantity of the gel fraction up to 15 min exposure. The position of the minimum shifts to the content of $\text{Fe}(\text{DMDTC})_3$ of 50 ppm (curves 4 in Figs. 1—4) with prolongation of the exposure time.

The structural changes in the investigated copolymer during irradiation in the presence of a constant amount of anthracene and varying trace amounts of metal complexes of varying valence are also indicated by varying characteristic absorption bands in the infrared and ultraviolet spectral regions.

The presence of oxidation products is confirmed by changes in the absorption bands at $\tilde{\nu} = 1699$, 1731, and 1720 cm^{-1} . The greatest decrease in absorbance with increasing content of $\text{Co}(\text{DMDTC})_2$ (Fig. 5) during irradiation was observed at $\tilde{\nu} = 1699$ cm^{-1} (vibration of the $\text{C}=\text{O}$ groups in unsaturated aldehydes). The effect of additions of $\text{Cu}(\text{DMDTC})_2$, $\text{Ni}(\text{DMDTC})_2$, and $\text{Fe}(\text{DMDTC})_3$ on the change in absorbance of this band is significantly smaller and the values of ΔA vary on the level of changes in butadiene-styrene rubber observed in the

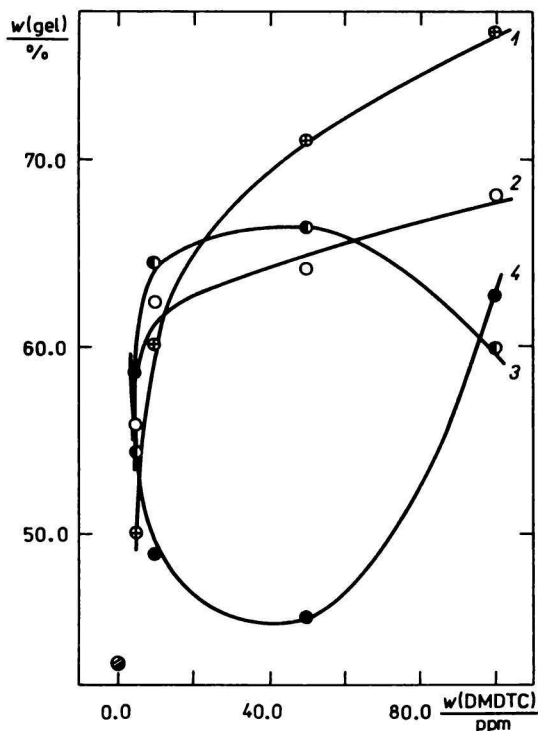


Fig. 4. Variation of the content of gel fraction w with amount of the added metal dimethyldithiocarbamate for constant irradiation time of BS films (60 min). The denotation is the same as in Fig. 1.

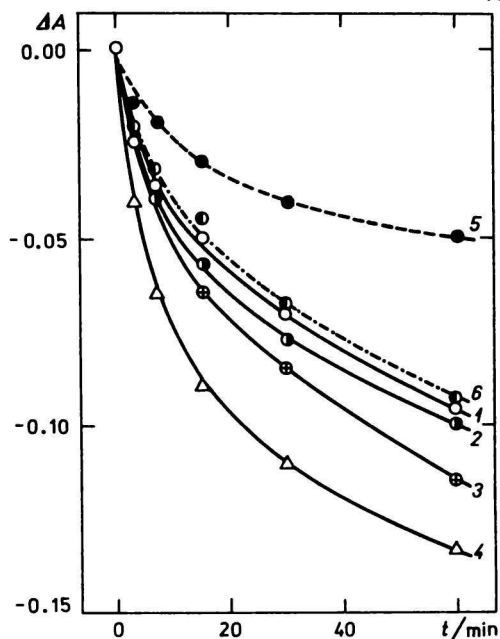


Fig. 5. Change in absorbance of the band at $\bar{\nu} = 1699 \text{ cm}^{-1}$ as a function of irradiation time of BS films with different additions of $\text{Co}(\text{DMDTC})_2$. 1. 5 ppm; 2. 10 ppm; 3. 50 ppm; 4. 100 ppm; 5. BS rubber without any addition; 6. BS rubber with 1 mass % of anthracene.

presence of 1 mass % of anthracene. The variation of the change in absorbance of the band at $\tilde{\nu} = 1731 \text{ cm}^{-1}$ (saturated aldehydes) with exposure time of the films with various additions of $\text{Ni}(\text{DMDTC})_2$ is represented in Fig. 6. The presence of anthracene and especially of anthracene with trace amounts of $\text{Ni}(\text{DMDTC})_2$ suppresses the formation of these compounds in BS polymer. The influence of other three investigated complexes on formation of saturated aldehydes is not so conspicuous.

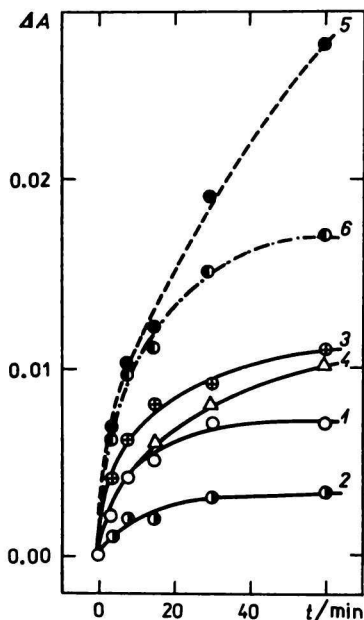


Fig. 6. Change in absorbance of the band at $\tilde{\nu} = 1731 \text{ cm}^{-1}$ as a function of irradiation time of BS films with different additions of $\text{Ni}(\text{DMDTC})_2$. The denotation is the same as in Fig. 5.

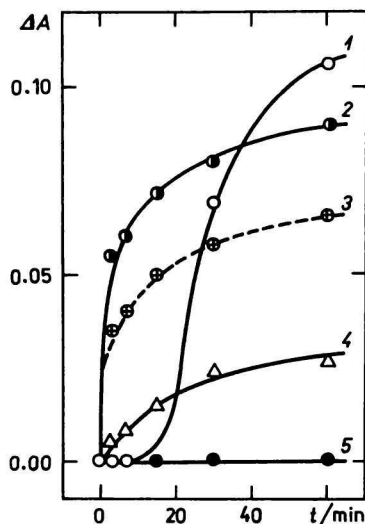


Fig. 7. Change in absorbance of the band at $\tilde{\nu} = 1720 \text{ cm}^{-1}$ as a function of irradiation time of BS films with addition ($w = 100 \text{ ppm}$) of metal dimethyldithiocarbamate. 1. $\text{Cu}(\text{II})$; 2. $\text{Co}(\text{II})$; 3. $\text{Ni}(\text{II})$; 4. $\text{Fe}(\text{III})$; 5. BS rubber without any addition.

The formation of saturated ketones during irradiation is affected by the investigated dimethyldithiocarbamates only if the addition of these substances exceeds 100 ppm (Fig. 7). In the presence of $\text{Fe}(\text{DMDTC})_3$ the formation of these compounds is fully suppressed during the whole interval of irradiation. $\text{Ni}(\text{DMDTC})_2$ also puts down the content of these products in comparison with pure copolymer, while $\text{Co}(\text{DMDTC})_2$ and $\text{Cu}(\text{DMDTC})_2$ increase the content of them. The sigmoid form of curve 1 after addition of $\text{Cu}(\text{DMDTC})_2$ is remarkable. Analogous course of formation of oxidation products was also observed in the presence of $\text{Cu}(\text{acac})_2$ [12].

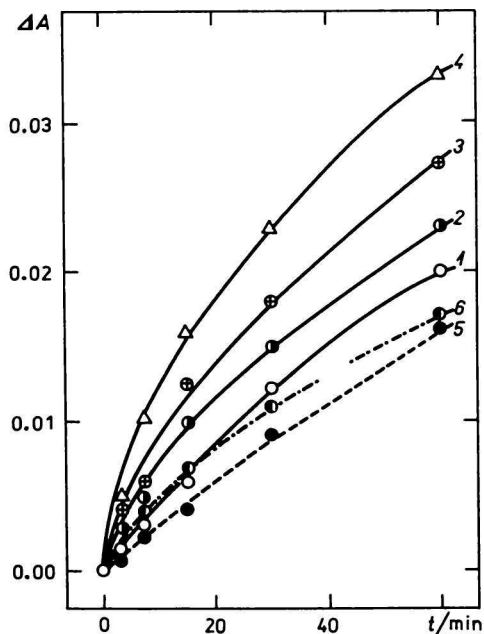


Fig. 8. Change in absorbance of the band at $\tilde{\nu} = 1070 \text{ cm}^{-1}$ as a function of irradiation time of BS films with different additions of $\text{Cu}(\text{DMDTC})_2$. The denotation is the same as in Fig. 5.

The increase in absorbance of the band at $\tilde{\nu} = 1070 \text{ cm}^{-1}$ is evidence of the formation of etheric bridges. The possibility of cross-linking of polymer chain through —O— is to the utmost favoured by an addition of $\text{Cu}(\text{DMDTC})_2$ (Fig. 8). The changes in absorbance of the bands at $\tilde{\nu} = 1595 \text{ cm}^{-1}$ corresponding to vibrations of the benzene rings as a function of irradiation time and amount of the added $\text{Cu}(\text{DMDTC})_2$ are represented in Fig. 9. The decrease in absorbance of this band with increasing irradiation time might indicate the opening of the benzene rings in polymer chain. Analogous changes are also produced by an addition of $\text{Co}(\text{DMDTC})_2$. The observed decrease in absorbance at this wavenumber is smaller for $\text{Ni}(\text{DMDTC})_2$ and $\text{Fe}(\text{DMDTC})_3$.

A relatively considerable change in absorbance appears at $\tilde{\nu} = 725 \text{ cm}^{-1}$ after addition of anthracene and complex metal compounds into BS rubber. This absorption band corresponds to skeletal vibrations of the main carbon chain. The dependence of ΔA of this band on irradiation time of films after additions of varying amounts of $\text{Cu}(\text{DMDTC})_2$ into BS rubber is represented for illustration in Fig. 10. The observed decrease in absorbance of the investigated samples shows that not only cross-linking of polymer macromolecules but also oxidation and accompanying breaking of the main chain takes place in the course of irradiation.

The catalytic activity of individual investigated dimethyldithiocarbamates concerning a decrease in unsaturation of the polymer chain is to be perceived

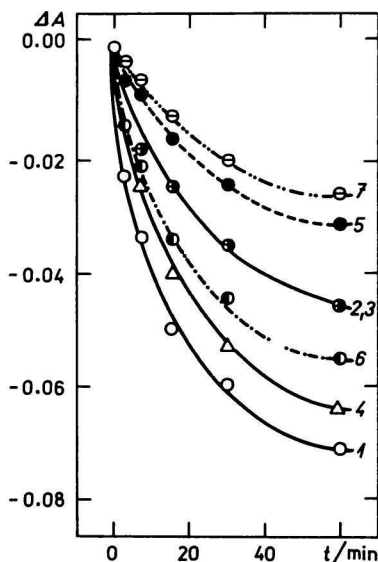


Fig. 9. Change in absorbance of the band at $\bar{\nu} = 1595 \text{ cm}^{-1}$ as a function of irradiation time of BS films with different additions of $\text{Cu}(\text{DMDTC})_2$. 1.—6. are the same as in Fig. 5. 7. BS rubber with $\text{Cu}(\text{DMDTC})_2$ ($w = 50 \text{ ppm}$) and without anthracene.

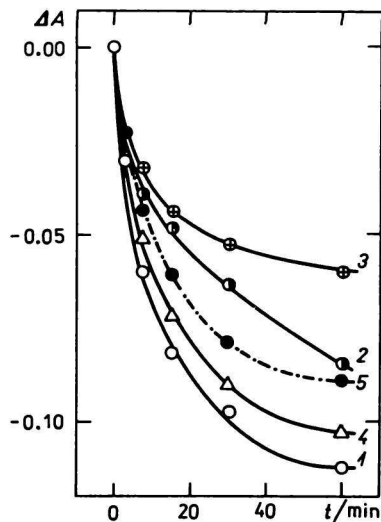


Fig. 10. Change in absorbance of the band at $\bar{\nu} = 725 \text{ cm}^{-1}$ as a function of irradiation time of BS films with different additions of $\text{Cu}(\text{DMDTC})_2$. 1. 5 ppm; 2. 10 ppm; 3. 50 ppm; 4. 100 ppm; 5. BS rubber with 1 mass % of anthracene.

from the change in absorbance of the band at the wavelength 382 nm (corresponding to the decrease in the unsaturated fundamental polymer chain) after addition of varying amounts of complexes of the used metals into BS rubber because this band corresponds to the $\text{C}=\text{C}$ bonds in the main polymer chain (Fig. 11). It results from this figure that the greatest decrease in absorbance was observed after addition of $\text{Ni}(\text{DMDTC})_2$ (Fig. 11, curve 1). Individual curves are consistent with the found content of gel fractions (Fig. 4).

The valuated absorption bands belong to the investigated copolymer because the contained additions of metal complexes are present only in trace amounts and the characteristic vibrations of these admixtures cannot be determined by the applied method and instruments.

On the basis of the obtained experimental results and literature data we can state that all investigated dimethyldithiocarbamates of the metals of variable valence exhibit catalytic activity in the photocross-linking process taking place in BS rubber in the presence of anthracene as a cross-linking agent.

It results from the presented relations that the rate and efficiency of cross-linking of BS copolymer in the presence of anthracene is mainly affected by the

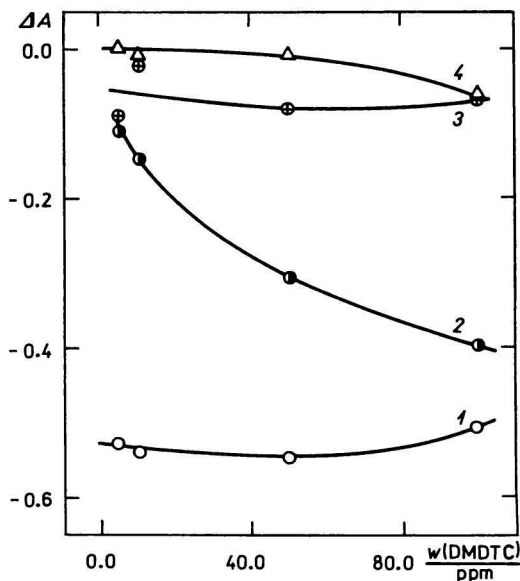


Fig. 11. Change in absorbance of the band at $\lambda = 382$ nm as a function of varying addition of metal dimethyldithiocarbamate after 60 min irradiation of BS films. 1. Ni(II); 2. Co(II); 3. Cu(II); 4. Fe(III).

central metal atom of the complex compound that catalyzes the splitting of endoperoxides of anthracene during irradiation to produce reactive oxygen radicals able to give rise to branching and cross-linking of the polymer chain in further stage of reaction. The contribution of ligand to realization of structural transformations is specific for every investigated compound because of different electronic structure of the central metal atom.

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