

Photodegradation of *cis*-1,4-Polyisoprene Sensitized by the Addition of Chloronitroso Compounds

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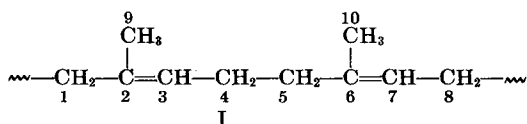
Synopsis

It was found that chloronitroso compounds with a free non-conjugated nitroso group show a considerable sensitizing activity in respect to the process of photochemical degradation of dissolved *cis*-1,4-polyisoprene, which is induced by visible radiation (4000-7000 Å.). The effect of 10 chloronitroso sensitizing compounds were investigated. The highest sensitizing activity was found with compounds 2,2-chloronitrosopropane and 1,1-chloronitrosocyclohexane. The maximum wavelength, of which the decrease of relative viscosity of solutions was the highest, was determined for 2,2-chloronitrosopropane. The highest sensitizing activity of chloronitroso compounds was found for wavelengths corresponding to the absorption maximum of the sensitizer added. The theory of the sensitizing activity of chloronitroso compounds is proposed.

Introduction

Photochemical degradation of polymers depends upon the wavelength and the related energy of radiation, intensity of light, structure of the polymer, and conditions of irradiation. Diene polymers are resistant to light (4000-8000 Å.). In the presence of oxygen these polymers are rapidly degraded by sunlight or ultraviolet radiation.¹⁻³ The ultraviolet radiation not only intensifies the oxidation reaction but also photodegrades the polymer. In an atmosphere free of oxygen in a polymer irradiated by ultraviolet radiation two parallel processes are observed, namely, photodegradation and crosslinking.^{2,4-6}

According to Dogadkin and Soboleva,⁷ the absorption of ultraviolet radiation increases the molecular energy to 78-100 kcal./mole. This energy may dissociate the C-C and C-H bonds. In the case of polyisoprene chains, the dissociation is facilitated by the decrease of energy of the bond at the methylene group, which is α to the double bond. The calculations of these authors have shown that for the chain I,



the energy of C-H bonds at C atoms 1,4, and 9 and at C atoms 5,8, and 10 is reduced by 19 kcal./mole, i.e., it is 78 kcal./mole. The stabiliza-

The low quantum yield of the degradation process is due chiefly to the conversion of absorbed energy of light quanta to heat and the low coefficient of light absorption of the polymer molecule.⁸ The quantum yield of the photodegradation of rubber by light in the region of 2500–4000 Å. is 4×10^{-4} .² The radiation energy at wavelength of 4000–8000 Å. is in general sufficient to produce the photochemical degradation of diene polymers, but the value of absorption coefficient of that radiation is very low, and therefore the quantum yield of photodegradation amounts to 10^{-5} – 10^{-6} . The photochemical reaction can be produced solely by radiation absorbed in the medium. From the theoretical point of view, certain modifications of the chemical constitution of the polymer may increase the coefficient of absorption for the determined wavelengths. This increase can be achieved by sensitization by addition of compounds which absorb these determined wavelengths and which can transfer the energy of absorbed quanta to the polymer macromolecule.

The investigations described in this paper have shown that chloronitroso compounds present a very interesting group of sensitizers for the photodegradation of polymers by low-energy visible radiation.

Experimental

Natural *cis*-1,4-polyisoprene was purified by fractionating three times from benzene solution with methyl alcohol in nitrogen atmosphere. The first and last fractions containing impurities were rejected.⁷

The effect of chloronitroso compounds on the solutions of *cis*-1,4-polyisoprene in benzene (0.3–1.0 wt.-% based on polymer) was examined by measuring the relative viscosity with the use of specially constructed viscometers operating in an oxygen-free atmosphere.⁹

Chloronitroso compounds were prepared by the method of Kosiński¹⁰ by passing pure chlorine into an aqueous solution of a stoichiometric mixture of ketone and hydroxylamine hydrochloride. In this way the following chloronitroso compounds were obtained: 2,2-chloronitrosopropane (I); 2,2-chloronitrosobutane (II); 2,2-chloronitrosopentane (III); 3,3-chloronitrosopentane (IV); 2,2-chloronitroso-4-methylpentane (V); 3,3-chloronitrosohexane (VI); 4,4-chloronitrosoheptane (VII); 1-phenyl-2,2-chloronitrosopropane (VIII); 1,1-chloronitrosocyclopentane (IX); 1,1-chloronitrosocyclohexane (X).

The purified chloronitroso compounds were added in the dark to the examined solutions of *cis*-1,4-polyisoprene by use of a gravimetric buret.

The benzene solutions of *cis*-1,4-polyisoprene with the chloronitroso compounds added were irradiated directly in the viscometer by use of a Philips 60276/1500 w./120 v. tungsten lamp or 1000 w./220 v. BGW photolamp. In order to obtain monochromatic light, interference filters were used. The measurements of relative viscosity were carried out in the dark at a constant temperature of $20 \pm 0.01^\circ\text{C}$.

Molecular weights were determined either viscometrically or by light scattering. The viscometric method¹¹ involved measuring the decrease

of viscosity in Ubbelohde viscometers. The viscometric molecular weight was calculated from the equation:¹²

$$[\eta] = 5.02M^{0.667}$$

In the light-scattering method the Peaker apparatus as described by Altgelt and Schultz¹³ was used. These measurements were carried out by M. Strzelecka and M. Kalfus.

The infrared spectra of *cis*-1,4-polyisoprene before and after degradation were determined with a Zeiss UR-10 spectrometer. The specimens for these measurements were prepared according to Kössler¹⁴ by casting thin rubber films from solutions on NaCl plates.

Results

The addition of chloronitroso compounds to benzene solutions of *cis*-1,4-polyisoprene produces a very rapid photodegradation of the polymer on exposure to light.

The measurement of molecular weight, compiled in Tables I and II, show that a very rapid degradation takes place immediately after the illumination. After 1 min. exposure to light in the presence of 2,2-chloronitrosopropane (I) or 1,1-chloronitrosocyclohexane (X), the average molecular weight of *cis*-1,4-polyisoprene with molecular weight of 2,466,000 decreases to 360,000. A decrease of the same order of magnitude of the average molecular weight from 2,466,000 to 450,000 in absence of chloronitroso compounds requires a 60 min. irradiation with ultraviolet radiation from a Hanau Q-700 lamp.

The viscometric examination of the variation of average molecular weight in another sample of *cis*-1,4-polyisoprene with the molecular weight of 732,000 (Table II) shows that the prolongation of exposure time does not affect essentially the further degradation of the polymer molecule.

It may be concluded from the relationship between the decrease of viscosity of *cis*-1,4-polyisoprene solutions and the wavelength of illuminating light that the greatest decrease of relative viscosity is produced by monochromatic light at a wavelength corresponding to the absorption maximum of the chloronitroso compound added. In the case of 1,1-

TABLE I
Average Molecular Weight of Natural *cis*-1,4-Polyisoprene in Cyclohexane by Light Scattering

Chloronitroso compound used	Molar ratio of chloronitroso compound to monomer	Type of radiation	Average molecular weight
None	—	None	2,466,000
None	—	Ultraviolet	450,700
I	1:10	Visible light	371,900
X	1:10	Visible light	366,200

TABLE II

Average Molecular Weight of Natural *cis*-1,4-Polyisoprene in Toluene by Viscometric Method. Chloronitroso Compound X Used, Molar Ratio X: Isoprene = 1:33

Exposure time (1000 w. light), min.	Average molecular weight
None	732,000
1	75,000
5	70,000
10	68,600
30	66,260
60	66,200

chloronitrosocyclohexane¹⁵ and 2,2-chloronitrosopropane (Fig. 1) the wavelengths are in the range of 6450–6550 Å. With increasing or decreasing wavelengths the decrease of viscosity of *cis*-1,4-polyisoprene solutions diminishes. Consequently the radiation produces a sensitized photo-degradation of *cis*-1,4-polyisoprene.

The relative viscosity of *cis*-1,4-polyisoprene solutions decreases more slowly, the lower the molar concentration of chloronitroso compound added. This effect increases with increasing size of the chloronitroso molecule (Figs. 2, 3, and 4).

The measurements indicate that the presence of oxygen and the addition of inhibitors (2,4-dinitrochlorobenzene, picric acid) do not affect at all the decrease of relative viscosity of *cis*-1,4-polyisoprene solutions which contain chloronitroso compounds. This fact suggests that in the reactions observed, free radicals formed by the simultaneous photolysis of chloro-

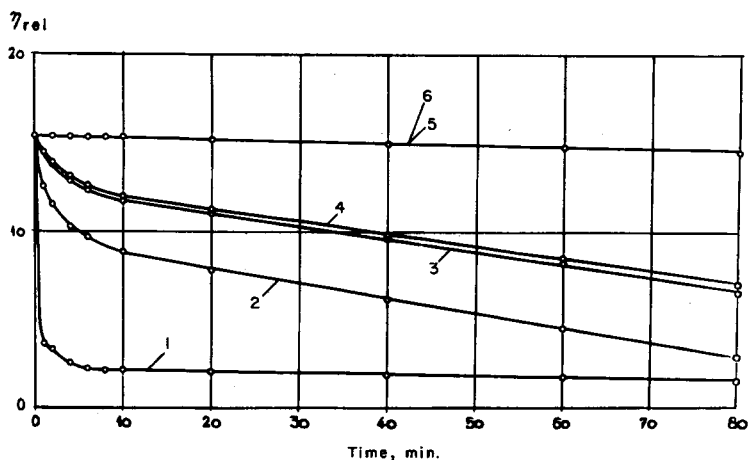


Fig. 1. Change of relative viscosity of 0.7 wt.-% benzene solution of *cis*-1,4-polyisoprene containing chloronitroso compound I, molar ratio I:isoprene = 1:33, on irradiation with light of various wavelengths: (1) 6500 Å.; (2) 6070 Å.; (3) 7300 Å.; (4) 5670 Å.; (5) 5000 Å.; (6) 4320 Å.

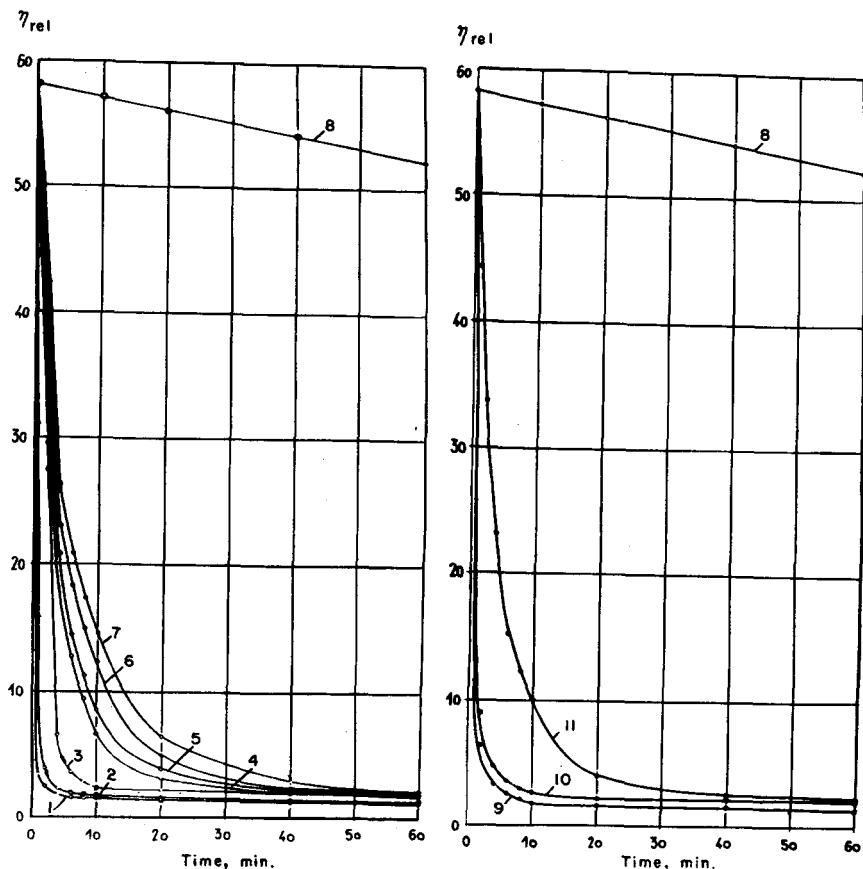


Fig. 2. Change of relative viscosity of 1.0 wt.-% benzene solution of *cis*-1,4-polyisoprene containing various chloronitroso compounds, molar ratio of chloronitroso compound: isoprene = 1:10: (1) with I; (2) with II; (3) with III; (4) with IV; (5) with V; (6) with VI; (7) with VII; (8) without any chloronitroso compound; (9) with X; (10) with IX; (11) with VIII.

nitroso compounds are not involved. It was found also that chloronitroso compounds are strong inhibitors of the radical polymerization of styrene and methyl methacrylate initiated by benzoyl peroxide; thus the photodegradation of *cis*-1,4-polyisoprene in solution cannot be due to the presence of radicals.

The products isolated from degradation in the presence of chloronitroso compounds consist of very viscous, semifluid substances.

The investigation of infrared spectra shows that during the sensitized photodegradation of *cis*-1,4-polyisoprene in the presence of chloronitroso compounds the basic structure of the polymer chain is not altered. Absorption spectra of the polymer degraded by exposure for 1 hr. to ultraviolet radiation from a Hanau Q-700 lamp with or without the addition of chloronitroso compounds are identical to those of the initial substance. No

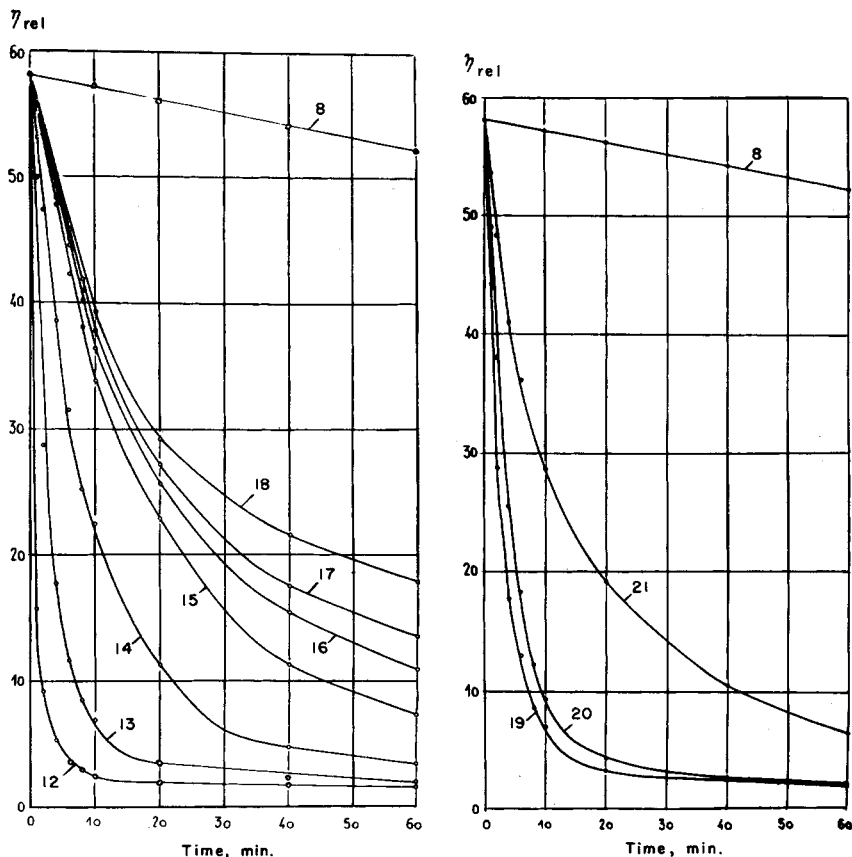


Fig. 3. Change of relative viscosity of 1.0 wt.-% benzene solution of *cis*-1,4-polyisoprene containing various chloronitroso compounds, molar ratio of chloronitroso compound:isohrene = 1:100: (8) without any chloronitroso compound; (12) with I; (13) with II; (14) with III; (15) with IV; (16) with V; (17) with VI; (18) with VII; (19) with X; (20) with IX; (21) with VIII.

new absorption bands which might indicate the possible cyclization of polymer molecules were found.

Discussion

Investigation of the effect of chloronitroso compounds on the solutions of polymers with various structures has shown that the rapid decrease of relative viscosity is found solely in the case of polymers with double bonds in the main chain.¹⁶ All diene polymers and copolymers belong to this group.

In order to explain the observed phenomenon of the sensitized photodegradation, the possibility of a donor-acceptor complex between the molecule of the chloronitroso compound and the polymer macromolecule was assumed. Measurements of dipole moments (carried out by Z. Malarski

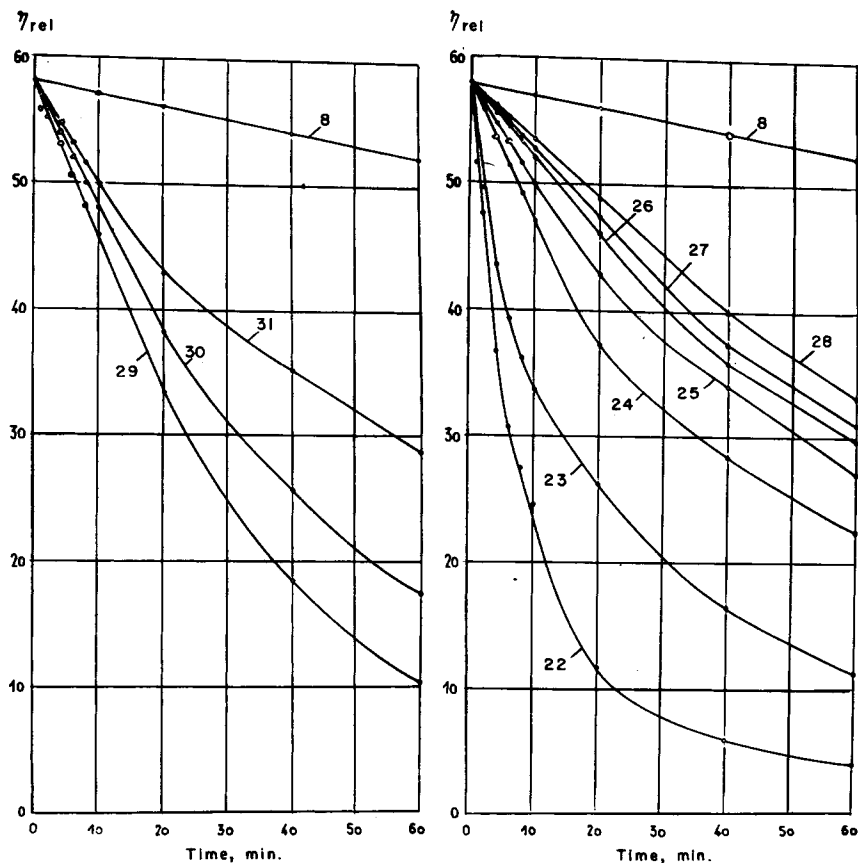


Fig. 4. Change of relative viscosity of 1.0 wt.-% benzene solution of *cis*-1,4-polyisoprene containing various chloronitroso compounds, molar ratio of chloronitroso compound:isoprene = 1:500: (8) without any chloronitroso compounds; (22) with I; (23) with II; (24) with III; (25) with IV; (26) with V; (27) with VI; (28) with VII; (29) with X; (30) with IX; (31) with VIII.

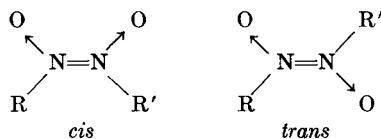
and J. F. Rabek) have shown that the stability of these complexes is not very high (Table III). The addition of a polar solvent, e.g., methyl alcohol, causes such complexes to decompose completely.

TABLE III
Dipole Moments of Chloronitroso Compounds

Chloronitroso compound	Dipole moment, Debye
I	2.48
II	2.49
IV	2.62
VIII	3.04
IX	2.78
X	2.84

The formation of the complex is due to the polarization of the double bond by the dipole of the nitroso group. The complex absorbs light within the same range of wavelengths in which the absorption maximum of the chloronitroso compound used is found. The absorption of light quanta changes the basic electronic state to one of the possible excited states. In this system the absorbed energy of light quanta is transferred directly to the bonds of polymer molecules and produces the observed photodegradation. The infrared spectra measured indicate that breaking of the chain is probably located between the isopentene groups and that it occurs simultaneously with the decomposition of the complex formed. In addition to the sensitized photodegradation produced by chloronitroso compounds and light in the polymer, there is photolysis of the sensitizers as well. The rates of both these reactions are different. The reaction of sensitized photodegradation takes place almost immediately after the illumination, whereas the photolysis of chloronitroso compounds proceeds slowly.¹⁷⁻¹⁹ The products of the simultaneous (photolysis) of chloronitroso compounds do not react either with the polymer molecule or its fragments.

The sensitizing effect of chloronitroso compounds is due chiefly to the nitroso group, which on account of the presence of the chlorine atom is not linked directly by any bond. The facility of the decomposition and photolysis of chloronitroso compounds is due to the presence of that group, which produces the characteristic blue coloration. Nitro compounds do not show a sensitizing activity, because their nitroso groups form colorless dimers.²⁰⁻²⁵



In order to split these dimers into monomers a temperature of 150–200°C. is necessary. In these conditions bluish-green (this color indicates the presence of a free nitroso group) short-lived monomers are formed, which undergo immediate rearrangement to form the corresponding oximes in accordance with the intramolecular disproportionation reaction.

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Résumé

On a trouvé que les composés chloronitrosés possédant un groupement nitroso libre non conjugué possèdent une activité sensibilisatrice considérable en ce qui concerne le processus de dégradation photochimique du *cis*-1,4-polyisoprène dissous, induite par la lumière visible (4000-7000 Å.) On a étudié l'influence de 10 composés sensibilisateurs chloronitrosés. L'activité sensibilisatrice la plus élevée a été trouvée avec le 2,2-chloronitrosopropane et le 1,1-chloronitrosocyclohexane. La longueur d'onde maximum, pour laquelle la diminution de viscosité relative des solutions est la plus élevée, a été déterminée pour le 2,2-chloronitrosopropane. On a trouvé que l'activité sensibilisatrice la plus élevée pour les composés chloronitrosés se situe aux longueurs d'onde, qui correspondent au maximum d'absorption due sensibilisateur ajouté. On propose une théorie de l'activité sensibilisatrice des composés chloronitrosés.

Zusammenfassung

Chlornitrosoverbindungen mit einer freien, nicht konjugierten Nitrosogruppe zeigen eine beträchtliche Sensibilisierungsfähigkeit für den photochemischen Abbau von gelöstem *cis*-1,4-Polyisopren bei Anregung mit sichtbarer Strahlung (4000-7000 Å.). Die Einwirkung von 10 Chlornitrososensibilisatoren wurde untersucht. Die höchste sensibilisierende Wirkung besaßen die Verbindungen 2,2-Chlornitrosopropan und 1,1-Chlornitrosocyclohexan. Die maximale Wellenlänge, bei welcher die stärkste Abnahme der relativen Viskosität der Lösungen auftrat, wurde für 2,2-Chlornitrosopropan bestimmt. Die höchste sensibilisierende Wirkung der Chlornitrosoverbindungen trat bei Wellenlängen auf, die dem Absorptionsmaximum des zugesetzten Sensibilisators entsprachen. Eine Theorie für die sensibilisierende Wirkung von Chlornitrosoverbindungen wird aufgestellt.

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