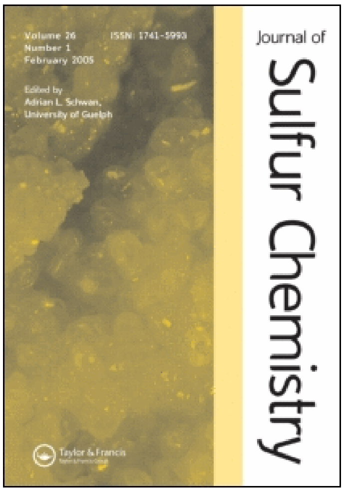

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Sulfur-organic Initiators Applied to Radical Polymerization

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SULFUR-ORGANIC INITIATORS APPLIED TO RADICAL POLYMERIZATION

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CONTENTS

The involvement of different sulfur-organic compounds in the initiation of radical polymerizations has been considered. Sulfides, disulfides, polysulfides, thiols, sulfenamides, and azo sulfides have been shown to generate radicals due to the cleavage of sulfur bonds. Sulfur-containing peroxides as well as thioacetals and thioketals have been chosen to illustrate the effect of sulfur upon the homolytic fission of different bonds such as C–O, O–O, and C–C. Numerous examples have been considered for the application of sulfur-organic compounds as components in redox systems, wherein the radicals initiating the polymerization are generated by oxidation or reduction of the sulfur-containing compounds involved.

Key words: Radical polymerization, initiation, sulfides, disulfides, thiols, sulfenamides, sulfur-organic peroxides, thioacetals, thioketals, azo sulfides.

1. INTRODUCTION

Sulfur-organic compounds and sulfur itself are applied in the chemistry of high-molecular compounds and, in particular, in radical polymerizations to play the role of monomers, molecular-weight regulators, cross-linking and chain transfer agents, inhibitors, and stabilizers of polymeric materials. Much less information has emerged about sulfur-containing initiators of polymerizations. However, a detailed study of the initiation processes is indispensable in the design of polymeric materials possessing the desired properties.

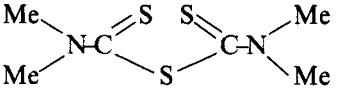
The present review is intended to cover the available data concerning the role of various sulfur compounds as polymerization initiators.

Here, we take no account of various applications of sulfur-organic compounds in the photoinitiation of polymerizations; besides, our considerations of their use as vulcanizers are only brief since these aspects have already been reviewed[1-5].

2. GENERATION OF RADICALS BY CLEAVAGE OF CHEMICAL BONDS

2.1. *Mono-, di-, and polysulfides.*

Organic sulfides have no practical use as initiators of polymerizations. However, *N*, *N*,*N'*,*N'*-tetramethylthiuram sulfide **1** initiates methyl methacrylate, styrene, acrylonitrile, and methacrylonitrile polymerizations at 95 °C[6].

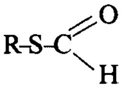


1

Compound **1** initiates also the bulk polymerization of styrene[7] its activity being inferior to that of both the conventional initiators such as azobisisobutyronitrile (AIBN) and dibenzoyl peroxide and to that of thiuram and benzothiazolyl disulfides.

Dithiocarbamates, for example *S*-methyl *N*,*N*-diethyldithiocarbamate, initiate the polymerization of methyl methacrylate, acrylonitrile, and vinylidene chloride[8]. Zinc *N*,*N*-diethyldithiocarbamate is an active initiator of the bulk polymerization of styrene[9]; dithiocarbamates of sodium, zinc, dialkylaluminium, piperidinium, etc., are used for curing rubber[3,10].

S-Alkyl thioformates such as **2** have been found to initiate the polymerization of vinyl monomers like methyl methacrylate and styrene[11].



$R = n\text{-}C_5H_{11}$

2

The polymerization of methyl methacrylate is also initiated by tetrakis(alkylthio)ethenes[11-13]; here, the reaction order of the initiator is 0.35, indicative of its combined initiating and inhibiting properties[14]. In addition to initiation, there occurs a chain transfer with organic sulfides[15,16].

Disulfides are known as initiators of radical processes. Thus, thiuram disulfides and dithioxanthates are used to accelerate rubber curing and to increase the thermostability of rubber[10,17-19]. Dibenzoyl disulfide decomposes at 70 °C to form radicals and, as a result, initiates vinyl polymerization[20]. A number of aromatic disulfides, e.g. diphenyl, dibenzyl, dibenzoyl, dinitrodiphenyl, dibenzothiazoyl disulfide and others, appear to be of low efficiency as thermal initiators for polymerizations[7,8,21-22]. Dibenzoyl disulfides possessing different para-substituents initiate emulsion copolymerizations of butadiene and styrene[20]. Hexachlorocyclotriphosphazene polymerization initiated by *N,N,N′,N′*-tetrapropylthiuram disulfide proceeds also by the radical mechanism[23]. To polymerize methyl methacrylate there has been used a modified poly-γ-benzylglutamate containing S-S bonds[24].

It should be noted that *n*-alkyl disulfides (i.e. dipropyl and di-lauryl disulfide) do not actually initiate radical polymerizations[25].

Bis(isopropoxythiocarbonyl) disulfide, *N,N,N′,N′*-tetramethylthiuram disulfide and dibenzothiazolyl disulfide initiate the polymerization of isoprene[12] and styrene[7] as well as the copolymerization of styrene with 1,3-butadiene[20,26]. *N,N,N′,N′*-Tetramethylthiuram disulfide has been reported to initiate the polymerization of styrene[27] and methyl methacrylate[28], of acrylonitrile and methacrylonitrile[6]. In the decomposition of disulfides sulfur-centered thiyl radicals are formed[12,29,30].

N,N,N′,N′-Tetramethylthiuram disulfide has been shown to decompose in a first-order reaction with 80–90% conversion[18]. Still, with thiuram disulfides as initiators the reaction order is determined by the disulfide structure in the equation derived for the polymerization rate[31].

In addition to polymerization initiation, disulfides participate in chain transfer processes[28].

With *N,N,N′,N′*-tetraethylthiuram disulfide[32,33], dibenzoyl disulfide[32], bis(isopropoxythiocarbonyl) disulfide[34], tetrathiaadamantyl disulfide and dibenzyl disulfide[35], polystyrene and poly-(methyl methacrylate) possessing sulfur-containing end groups have been prepared to allow a variety of further macromolecular reactions[33].

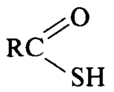
It has been shown that catalytic cleavage of an S-S bond in aromatic disulfides occurs at room temperature in the presence of electron acceptors such as aluminum and gallium bromide[36,37].

The polymerization of vinyl acetate[38] and styrene[39,40] proceeds in the presence of the cyclic disulfide 1-oxa-4,5-dithiacyclohexane.

Aliphatic tri-, tetra-, and polysulfides have been used to prepare chloroprene oligomers[41]. Dimorpholinyl tetrasulfide has been shown to be an accelerating and curing agent for rubber mixtures[10]. Bis-(*N,N*-pentamethylene)thiuram tetrasulfide initiates the bulk polymerization of styrene[27].

2.2 Thiols, sulfenamides and azo sulfides

Thiols can be used to initiate polymerizations. Thus, thiocarboxylic acids **3** have been shown to initiate the polymerization of methyl methacrylate and styrene in bulk and in benzene solution[42].



$RC(=O)SH$

R = Me, Ph **3**

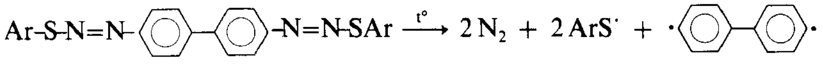
Mercaptoacetic and mercaptosuccinic acid have been employed in thermal polymerizations of methyl methacrylate, styrene, and acrylamide at 60 °C[43]. Lauryl mercaptan has been used as an initiator to copolymerize 1,3-butadiene and styrene[20,44,45].

With methyl methacrylate[46,47], MMA–RSH complexation has been shown to lead to a pronounced increase of the thermal polymerization rate.

The presence of aliphatic thiols causes a decrease of the rate of thermal styrene polymerization[48]; and the thiol consumption rate has been shown to be independent of its initial concentration[45,49].

The utilization of poly(γ-mercaptopropylsiloxane) absorbed on silica gel to initiate polymerization of acrylic acid[50] is in contrast to the inability of the low-molecular propanethiol to act as initiator.

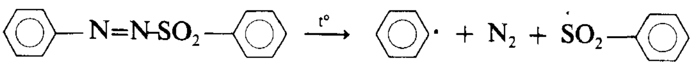
Compounds containing an S-N bond of low stability[12] are widely applied in the low-temperature structurization of rubber and as effective initiators of the polymerization of vinyl monomers[9,51–54]. Thus, for instance, biphenylyl-4,4′-bisazo bis(aryl sulfides) **4** initiate the polymerization of methyl methacrylate and acrylonitrile at 70 °C[54].



Homolytic decomposition to form two radicals and a molecule of nitrogen is typical of arylazo sulfides (ADAT)[52,53,55,56]:

$$Ar\text{-}N{=}N\text{-}SR \xrightarrow{t^\circ} Ar^{\cdot} + N_2 + RS^{\cdot}$$

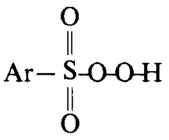
Phenylazo phenyl sulfone has been described as a source of free radicals[57]:



3. THE SULFUR EFFECT UPON THE CLEAVAGE OF DIFFERENT BONDS

3.1. Sulfur-organic peroxides

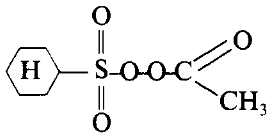
The presence of sulfur in a peroxide influences the breakdown of the peroxide bond. An investigation of arylsulfonyl hydroperoxides **5** has shown them[58] to be capable of initiating vinyl polymerization, e.g. of methyl methacrylate and acrylonitrile.



5

$$Ar-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{-}O\text{-}O\text{-}H$$

Acetyl cyclohexylsulfonyl peroxide **6** has been used in styrene polymerization[59].



6

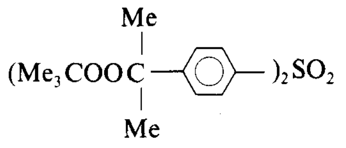
The sulfide-containing hydroperoxides **7** initiate styrene polymerization already at 5 °C[60].

$$R\text{-}S\text{-}R'\text{-}OOH \qquad R' = (CH_2)_m;$$

7

Water soluble hydroperoxide salts have been used to initiate emulsion polymerizations[61,62].

Because of their homolytic decomposition peroxides **8** and **9** have been used to prepare various polymer compositions[63,64]:



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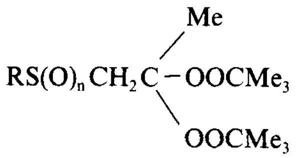
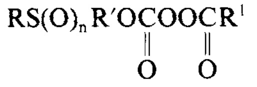


n = 1; 2 **9**

Compounds containing a group near the peroxide moiety such as *t*-butyl [*o*-(*t*-butylthio)phenyl] perbenzoate are also capable of initiating the radical polymerization of styrene and methyl methacrylate[65–67].

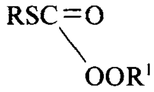
Sulfur-containing peroxycarbonates such as **10** initiate the polymerization of vinyl acetate, methyl methacrylate, and some other monomers at 50 °C[68].



$RS(O)_nR'O\underset{\underset{O}{\|}}{C}OO\underset{\underset{O}{\|}}{C}R^1$

n = 0, 2

10



11

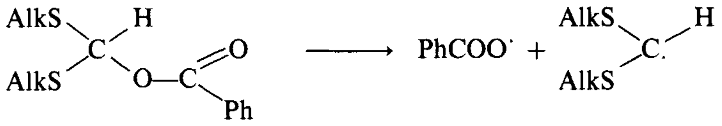
Peresters of *S*-alkylcarbonic acids **11** are only stable below 0 °C. They initiate the polymerization of styrene and vinyl chloride[69] and exert practically no influence upon the chain transfer processes.

Therefore, the stabilities of sulfur-organic peroxides and their activity in radical processes are determined by the following factors:

(i) the relative position of the sulfur and the peroxide group; generally, the farther apart they are positioned, the more stable is the peroxide;
(ii) the oxidation state of the sulfur atom: the higher it is, the more stable is the peroxide;
(iii) possible inter- and intramolecular interactions, often leading to lowered peroxide stability;
(iv) the effect of sulfur upon the mechanism of decomposition; a polar medium or the presence of polar species favors usually the heterocyclic decomposition of peroxides.

3.2. Cleavage of different bonds

Oxygen-containing thioacetal derivatives such as 1-benzoyl-oxy-1,1-bis(alkylthio)-methanes **12** can exhibit initiating properties[11,13], resulting in the formation of benzoyloxy and bis(alkylthio)methyl radicals:



12

Tetrakis(arylthio)methanes and -ethanes have been described as polymerization initiators[70]. An ability to initiate vinyl polymerization, e.g. of methyl methacrylate, has been observed with tetrakis(alkylthio)-ethanes[11,13].

4. SULFUR-ORGANIC COMPOUNDS AS COMPONENTS OF INITIATING SYSTEMS

Sulfur-organic compounds have a variety of applications as components of redox systems where they can function as both oxidizing and reducing agents. Persulfates are well-known as oxidative components of redox systems. However, their interactions with reducing agents most often result in cleavage of the peroxide bond without reduction of sulfur-containing groups. There are some surveys reporting various utilizations of persulfates for both preparation of polymers and for their modification[71-75]. This section considers organic sulfur compounds which are involved in redox reactions.

4.1. Thiols and thioureas

Thiols are widely employed to initiate the decomposition of oxidative radical starters. Components such as lauryl mercaptan[76,77], thiomalonic[78,79], thiomalic[80-84], mercaptosuccinic[47], and mercaptoacetic[47,85,86] acid, 2-mercaptoethanol[87,88], 2-mercaptoethylamine[89], and cysteine hydrochloride[90] can be used to initiate persulfate decomposition and to promote monomer polymerizations in aqueous solution or emulsion[91-94]. Mercaptoacetic, thiomalic, and thiolacetic acid accelerate acrylonitrile polymerization initiated with peroxymonosulfate[95].

2-Aminoethanethiol has been observed to render active assistance in peroxydiphosphate initiated polymerizations[96,97].

Metal ions can become useful as oxidative components in combination with thiols. Thus, in the presence of a thiol the acrylonitrile polymerization rate increases appreciably upon addition of cerium(IV) ions[98-103]. In the case of 2-mercaptoethanol the polymerization rate is proportional to $[\mathrm{Ce}]_0^{0.4}\cdot[\mathrm{RSH}]_0^{0.5}$[99]. With thiomalonic acid a complex results which decomposes to the radicals initiating the polymerization[98]. For polymerizations initiated with the Ce^{4+}–2-propanethiol system the reaction orders of its components are 0.5 and the initiating radical $\mathrm{Me_2CHS}^{\cdot}$ appears with the decomposed oxidant-reductant complex[104].

Manganese(III) laurate has been used as oxidant[105,106]. The system $\mathrm{KBrO_3}$-mercaptoacetic acid had been used to initiate acrylonitrile polymerization[107] and that of methyl methacrylate[108,109] as well as their graft copolymerization to natural rubber[110]. A combination of $\mathrm{KBrO_3}$ and thiomalic acid has been used to polymerize methyl methacrylate[111]. The methyl methacrylate polymerization rate in the presence of the vitamin B_{12}–2-mercaptoethanol system[112] has been found proportional to $[B_{12}]_0^{0.5} \cdot [RSH]_0^{0.5}$.

Systems such as ammonium metavanadate–mercaptosuccinic acid[113], potassium permanganate–mercaptoacetic[114] or mercaptosuccinic[115] acid have been described in connection with the polymerization of acrylamide and methacrylamide. The following systems have been shown to be highly effective for methyl methacrylate polymerization[116]: chlorine–thioglycolic acid, bromine–2-mercaptoethanol, the system iodine–2-mercaptoethanol being inferior to the former ones.

Polymerization initiated with H_2O_2[117,118] and hydroperoxides[119] in the presence of thiols allow a temperature decrease due to the initiation systems formed:

$$RSH + R^1OOH \rightleftharpoons [\text{complex}] \longrightarrow RS^{\cdot} + R^1O^{\cdot} + H_2O$$

The systems 2-phenyl-2-propyl hydroperoxide (or dibenzoyl peroxide)–2-mercaptobenzothiazol have been used for the structurization of rubber solutions[120,121]. The methyl methacrylate graft copolymerization is initiated with the system H_2O_2-cysteine[122]. The decomposition rate of *t*-butyl hydroperoxide is increased by three orders of magnitude in the presence of triazinedi- and -trithiols as well as of their zinc and copper salts[123].

There exist systems containing sulfur dioxide as an oxidant[120,121] the interactions of which with thiols result in polymerization initiating radicals.

The reaction of aliphatic thiols with peroxide initiators leads to a lower rate of styrene polymerization[124]. In the presence of RSH the effective constant of the dibenzoyl peroxide decomposition rate increases[46,48].

With the systems dibenzoyl peroxide or *t*-butyl perbenzoate with aliphatic thiols the polymer molecular weight and polydispersity are determined by the involvement of the thiol in the initiation, chain transfer, and interactions with the initiator[125].

Systems of different alkanethiols with lauryl peroxide have been utilized to prepare polyacrylamide and polyacrylonitrile with sulfur-containing end groups[126] and that of thiophenol with lauryl peroxide to prepare poly-(methyl methacrylate)[127].

The systems *t*-lauryl mercaptan–dibenzoyl peroxide, 2-phenyl-2-propyl and 1-phenyl-1-cyclohexyl hydroperoxide, AIBN have been used to graft styrene, methyl methacrylate, and acrylonitrile to 1,4-*cis*-poly(butadiene)[128] and to polymerize chloroprene[129].

Studies of styrene polymerization initiated with dibenzoyl peroxide in the presence of *n*- and *t*-lauryl mercaptan have shown the RSH effect upon the polymerization to be observable for conversions above 3%[130,131].

Thiols can also induce decomposition of initiators other than peroxides[132,133]. The effect of lauryl mercaptan upon the AIBN decomposition has been considered in an optimization of methyl methacrylate polymerization[132]. As stated in the literature[133], one should take into account the interactions of thiols and initiators while estimating the constants of chain transfer to RSH. The presence of 2-mercaptobenzothiazole[134], mercaptoacetic and mercaptosuccinic acid[43] lowers the rate of methyl methacrylate polymerization initiated with AIBN.

Thiourea has been widely employed in redox systems to initiate polymerization[135]. Low reaction temperatures and activation energies are inherent to such systems.

In the presence of thiourea there is observed an increase in the rate of methyl methacrylate polymerization initiated with potassium persulfate[136].

The system thiourea-potassium peroxydiphosphate has been applied to graft copolymerization of methyl methacrylate to wool fibres[137,138] and silk[139]. Potassium bromate[110,140-143] and halogens[144] are often used as oxidants. However, the iodine systems have been reported to be of low efficiency in the initiation of polymerization.

The system thiourea-H_2O_2 has been widely applied to graft copolymerization[145-151] and polymerization of acrylonitrile[145] and methyl methacrylate[146].

The system thiourea-dibenzoyl peroxide has been described in connection with methyl methacrylate polymerization[146]. There have been carried out detailed studies of styrene polymerization in benzene in the presence of cumyl hydroperoxide and its mixtures with *N*-benzoyl-*N'*-(*n*-propyl)- and *N*-benzoyl-*N'*-isobutylthiourea[152].

The system thiourea–$KMnO_4$ has been used to polymerize methyl methacrylate[136] and acrylonitrile[153]. Initiating systems of thioureas with transition metal ions such as Mn^{3+} [154,155], Ce^{4+} [103,156-160], V^{5+} [161-167], Cr^{6+} [168], and Fe^{3+} [169-175] have been utilized on a large scale.

It has been also noted that the replacement of thiourea hydrogens by alkyl groups leads to a decreasing polymerization rate in systems containing metal ions[174,175].

Vinyl polymerizations initiated with systems including *N*-alkyl(aryl)thioureas such as dibenzoyl peroxide and *N,N'*-diphenylthiourea[149,176] and *t*-butyl hydroperoxide and *N,N,N',N'*-tetramethylthiourea[177] have been investigated.

N-Methylthiourea has been used as a component of redox systems. For acrylonitrile polymerization, its systems with Mn^{3+} [178], Cr^{6+} [179], Ce^{4+} [103], potassium bromate[180], potassium peroxydiphosphate[181], and potassium permanganate[182] have been used. The system H_2O_2–thiourea dioxide–Fe^{2+} has been described in connection with the polymerization of glycidyl methacrylate[183,184].

4.2. *Sulfides and disulfides*

Organic sulfides have not been utilized as components of redox systems. Their interactions with H_2O_2 and other peroxides lead to fast peroxide consumption for the oxidation of sulfur atoms and, as a consequence, to inhibition of polymerization[185,186].

However, radicals have been observed to form in the course of hydroperoxide and R_2S interactions[187], their yield being low due to the occurrence of a number of parallel homo- and heterolytic reactions[188,189].

Dialkyl (or diaroyl) peroxides readily react with sulfides to oxidize the latter to sulfoxides[186,190,191]. Still, Horner and Jürgens report[190] that this reaction can proceed by both an ionic and a radical mechanism. The radical reaction route results in the substitution of hydrogen atoms in the α-position to sulfur[192].

In the presence of copper salts as catalysts the substitution becomes dominant[191,193-195] and thus can be considered as a potential preparative method for the synthesis of α-substituted products. In the case of thioacetals the hydrogen atoms are more active than those in sulfides; benzoyloxy substituted thioacetals have been observed as main reaction products with benzoyl peroxide[196].

In vinyl polymerization initiated with benzoyl and lauroyl peroxide, geminal bissulfides not only fail to inhibit the process, but even increase the polymerization rate[11,13]. The initiating activity of the above systems is explained by the emergence of a number of reaction products which in turn initiate polymerization. It is important to note that 1,3-bissulfides inhibit polymerization[197].

Some other systems involving sulfides are known to initiate polymerization. Thus, for instance, diphenyl sulfide is poorly oxidized by peroxides[190], while its presence gives a pronounced increase in the rate of methyl methacrylate polymerization initiated with dilauroyl peroxide[127].

The S-S bonds have been already stated to cleave at higher temperatures. Various activators have been used for disulfide decompositions. Bis-(*N,N,N′,N′*-tetraalkyldiamidophosphoryl) disulfides have been studied with respect to rubber curing[198]; in the presence of peroxides and sulfenamides they readily decompose to reactive $RS^{\cdot}$ radicals. The system thiocarbamoyl sulfenamide-dibenzothiazolyl disulfide has been shown to markedly accelerate rubber curing with sulfur[199].

Polystyrene modified with *N,N,N′,N′*-tetramethylthiuram disulfide in the presence of peroxides has been found to decompose at higher temperatures than an unmodified sample[200].

Dibenzothiazolyl disulfide reacts only slowly with hydroperoxides[12]; however, upon addition of diphenylguanidine or 1-naphthylphenylamine the reaction is accelerated and the disulfide is reduced already at 20 °C.

The decomposition of disulfides can also be activated by nitrogen containing compounds. For example, the system diisopropylthiophosphoryl di(or tetra)sulfide and dimorpholinyl disulfide has been applied to polyisoprene curing[201].

Disulfides by themselves can activate the decomposition of other initiators. They have been observed to considerably accelerate styrene emulsion polymerization initiated with persulfate[20]. The use of systems incorporating diisopropylxanthate disulfide and H_2O_2 or dibenzoyl peroxide has been described for the emulsion and bulk polymerizations of styrene[93].

In the presence of disulfides peroxides decompose by the radical mechanism. Thus, the reactions of diphosphoryl disulfides and diisopropylxanthate disulfide with *t*-butyl hydroperoxide proceed slowly at 70 °C while they occur readily with UV irradiation[202].

Transition metal salts are also utilized to activate disulfide decomposition. For example, the systems diphenyl disulfide-urea, diphenyl disulfide-cupric chloride as well as the ternary system PhSSPh-urea-$CuCl_2$ have been reported to initiate methyl methacrylate polymerization[203,204].

The investigation of AIBN initiated polymerization of styrene in the presence of disulfides[205] has shown that aromatic disulfides decrease the polymerization rate appreciably, in contrast to aliphatic disulfides.

With thiuram disulfides[31] such as *N,N,N′,N′*-tetramethyl-, *N,N,N′,N′*-tetraethyl-, and *N,N,N′,N′*-tetrabutylthiuram disulfide one can observe a decrease of the rates of AIBN initiated polymerizations. With diisopropylxanthate disulfide heated in benzene in the presence of AIBN, interaction between the dimethylcyanomethyl radicals and the disulfide has been shown to lead to the formation of xanthate radicals[206].

4.3. Sulfoxides and sulfur-containing azo compounds

In initiating systems sulfoxides can work as both oxidants and reductants. Thus, systems such as dimethyl sulfoxide (DMSO)-thiol have been used to initiate methyl methacrylate polymerization in benzene solution[207,208].

The most important property of sulfoxides has been assumed to be their aptitude for the complexation of metal ions, a property which allows further involvement of sulfoxides in the redox initiation of polymerization. The systems of $MoCl_3$ with dialkyl sulfoxides[209], diphenyl sulfoxide[210], and polymeric sulfoxides[211] have been studied in methyl methacrylate polymerization.

Sulfoxides can also act as reductants in redox systems. For example, DMSO effectively initiates acrylonitrile polymerization in the presence of Ce^{4+} [212]. Acrylonitrile polymerization has been studied with the initiating system Mn^{3+}-DMSO[213-215].

Sulfoxide complexes, e.g. with metal salts, have been observed to take part in the initiation of polymerizations[216,217]. The addition of a dihexyl sulfoxide-$CoCl_2$ complex allows a pronounced increase in the rate of methyl methacrylate polymerization initiated with 4,4-dimethyl-1,3-dioxanyl hydroperoxide[218]. An increased rate of methyl methacrylate polymerization has been observed with the system 4-phenyl-1,3-dioxanyl hydroperoxide with the dicyclohexyl sulfoxide-$CoCl_2$ complex[219].

Sulfoxide complexes of metals can form initiating systems with methyl AIBN, too. Complexes of DMSO with Rh(III) and Ru(II) salts have been used for methacrylate polymerizations initiated with AIBN[220,221].

The use of sulfoxide-metal complexes capable of functioning as oxidants have been also assumed to lead to initiation of polymerizations. For instance, the rate of methyl methacrylate polymerization increases in the presence of the oxalic acid-$[Fe(DMSO)_6](ClO_4)_3$ system[222]. The polymerization of methyl methacrylate is accelerated in the presence of the complex $[Fe(DMSO)_6](ClO_4)_3$ and sodium cyanide[223].

It has already been mentioned that sulfur-containing azo compounds are not widely utilized as initiators because of their low initiating activity which can be increased by the use of certain additives inducing their decomposition[56,57].

4.4. *Various sulfur compounds*

As reported by many research workers, sulfonic acids are often utilized as emulgators to accelerate the polymerization of various monomers. Thus, sodium dodecanesulfonate facilitates persulfate decomposition[224,225] and gives a complex with the monomer in the emulsion polymerization of styrene[226]. The presence of a sulfonic acid leads to an increased rate of acrylamide polymerization[227] with a correspondingly lower activation energy[228].

In addition to the interactions of surface active species with initiator and monomer, certain physical factors can be responsible for polymerization acceleration[228].

Hydroperoxides are known to decompose into radicals more intensively in the presence of acids including *p*-toluenesulfonic acid[229]. In the polymerization of methyl methacrylate, styrene, and ethyl methacrylate both sodium metabisulfite and the system metabisulfite-sulfonic acid have been reported to initiate the process[230].

The application of the system [4-isopropylcumyl hydroperoxide-sodium formaldehyde sulfoxylate-complex of Fe(II) with *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetic acid] has been described for the emulsion polymerization of 1,3-butadiene[231].

The mixed-ligand complexes of Mn(III) acetylacetonate with aromatic sulfonic acids[232] have been considered of interest because of their properties as initiators and emulgators[233].

Sulfur compounds containing amino or amide groups have been also utilized as components of initiating systems. Thus, for example, the system sulfenamide-zinc dithiocarbamate exhibits curing activity and stabilizing properties for rubber[234]. The interaction of *para*-substituted thiobenzamides with $Fe(ClO_4)_3$ results in radicals initiating methyl methacrylate polymerization[235].

Studies of the effect of phenothiazine upon the AIBN initiated polymerization of methyl methacrylate have shown stable cation radicals to be formed with subsequent polymerization initiation, however, with a low rate[236,237].

The system 2,2′-thiodiethanol-trichloroaquabipyridyl-manganese(III) allows an increased rate of methyl methacrylate and acrylonitrile polymerization[238].

The polymerization of methyl methacrylate in the presence of the system *N*,*N*-dimethylaniline–*p*-toluenesulfonic acid chloride follows a radical mechanism and its initiation proceeds via decomposition of the chain transfer complex[239]. Methyl methacrylate radical polymerization can be initiated by the complex of oxalic acid with potassium ethylxanthate[240].

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