The effect of aliphatic sulfides on the photopolymerization of diacrylates

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Taking into account the possible advantages of the introduction of thioether bonds into the polymerization product, the polymerization of formulations based on 1,4-butanediol diacrylate or 1,6-hexanediol diacrylate and containing additives of various linear sulfides or cyclic dithioacetals was investigated to discover the influence of sulfides on the polymerization rate and yield. A commercial photofragmentating initiator was applied. It was found that the observed effect is the result of accelerating and retarding processes occurring simultaneously and their relationship and the extent of the effect depended on the reaction conditions and the sulfide structure. A schematic representation of the most important reactions is given.

(Keywords: photopolymerization; diacrylates; photofragmentating initiator; aliphatic sulfides; cyclic dithioacetals; hydrogen abstraction; chain-transfer)

INTRODUCTION

The introduction of an aliphatic sulfide group into an acrylate-based u.v.-curable formulation both with an additive and as part of a monomer may be advantageous for the polymerization product. First, it will improve the thermo-oxidative resistance of the resulting coating[1–4] since aliphatic sulfides are known thermo-oxidative stabilizers; the stabilization is achieved by non-radical decomposition of hydroperoxides caused by the oxidation products of sulfides[5–7]. Moreover, the presence of the sulfide groups in the polymerization product may improve its hydrophobic properties and increase its refractive index due to the presence of strongly polarizable sulfur atoms. All these properties are very important in electronic applications of poly(diacrylates)[8].

In addition to their anti-oxidative function, aliphatic compounds containing a thioether group were used as polymerization inhibitors during the preparation of acrylic monomers[9] and tested as stabilizers of u.v.-curable formulations[10]. Since they can act also as hydrogen donors and chain-transfer agents with the activity depending on their structure[11,12] their addition to a formulation may influence the polymerization rate and yield.

Our previous papers were devoted to the influence of aliphatic sulfides on the photopolymerization of 1,4-butanediol dimethacrylate initiated by benzophenone[13] and to the effect of the thioether linkage present in a dimethacrylate monomer on its polymerization induced by photofragmentating, hydrogen abstraction type and thermal initiators[14]. The results obtained indicate that the sulfide group may exert a positive or a negative effect on the polymerization rate and yield depending on the polymerization conditions. Generally, at moderate temperatures in air-saturated systems the introduction of the thioether bond into the monomer or additive molecule markedly enhances the rate and yield of the photopolymerization of dimethacrylates in comparison to a formulation free of sulfide groups or containing analogous compounds with ether groups, due mainly to the suppression of oxygen inhibition.

This paper deals with the photopolymerization of diacrylates. The aim of the work was to elucidate the influence of aliphatic sulfides on the polymerization of diacrylates induced by means of photofragmentating initiators, and to explain the mechanism of action of sulfides on the course of polymerization of multi(meth)acrylates. As model monomers 1,4-butanediol diacrylate (BDDA) and 1,6-hexanediol diacrylate (HDDA) were chosen. The work is part of a continuing investigation of the influence of the thioether bond on the polymerization of multiacrylates.

EXPERIMENTAL

Materials

BDDA (Merck-Schuchard, Hohenbrunn, Germany) and HDDA (Aldrich Chemical Co. Ltd, Gillingham, UK) were purified from the inhibitor by passing through a column with basic alumina (Merck, Darmstadt, Germany). Irgacure 184 (1-benzoyl-1-cyclohexanol, BCH; Ciba-Geigy, Basel, Switzerland) and 2-dimethylamino-ethanol (DMAE; Koch-Light Lab., UK) were used as received. Di-n-propyl sulfide (Pr_2S) obtained from n-propyl bromide and Na_2S was distilled three times[15]. Di-n-propyl sulfoxide (Pr_2SO) was obtained from Pr_2S by oxidation with H_2O_2 in glacial acetic acid according to a general procedure given elsewhere[16].

Di-n-butyl thiodipropionate (DBTP) was synthesized by direct esterification of thiodipropionic acid with n-butanol in toluene in the presence of *p*-toluenesulfonic acid. *β*-2,4,6-Trimethyl-1,3,5-trithiane (TMT, *cis–cis* form), *β*-2,4,6-triphenyl-trithiane (TPT, *cis–cis* form) and 2,4,6-trimethyl-2,4,6-triphenyl-1,3,5-trithiane (TMTPT) were obtained from H_2S or $Na_2S_2O_3$ and the corresponding

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aldehyde or ketone according to references 17 and 18 and were purified by repeated crystallization.

All the sulfur-containing additives showed a similar very low residual absorption in the irradiation region.

Polymerization

The polymerization was carried out in 25 mm diameter glass vials thermostatted with distilled water. Each vial contained 0.5 ml of the reaction mixture. The light source (110 W medium-pressure mercury lamp ASH 400 D4 from Astralux, Vienna, Austria) equipped with a glass filter was placed 10 cm from the bottom of the vials. The transmitted light was in the range 325–410 nm with λ_{max} at 366 nm. Argon (0.0005% O_2 content) was passed through the samples for 3 min, prior to irradiation, as required. The polymers obtained were purified by chloroform extraction. The monomer conversion was determined gravimetrically. None of the additives used was able to initiate polymerization during thermal treatment at 40–80°C without irradiation.

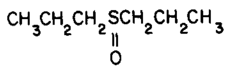
Swelling

The samples for the swelling measurements were prepared by polymerization of 1 ml of the formulation investigated under Ar at 40°C for 3 min. The swelling measurements were performed at room temperature.

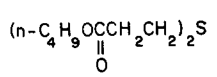
RESULTS AND DISCUSSION

The polymerization of BDDA and HDDA was carried out in the presence of a number of sulfur-containing additives of various structures listed below:

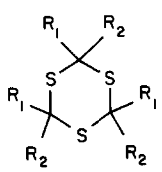
$CH_3CH_2CH_2SCH_2CH_2CH_3$ Pr_2S



$CH_3CH_2CH_2\underset{\underset{O}{\|}}{S}CH_2CH_2CH_3$ Pr_2SO



$(n\text{-}C_4H_9O\underset{\underset{O}{\|}}{C}CH_2CH_2)_2S$ DBTP



TMT: R_1 = H-, R_2 = CH_3-

TPT: R_1 = H-, R_2 = C_6H_5-

TMTPT: R_1 = CH_3-, R_2 = C_6H_5-

These compounds were chosen for the following reasons:

Pr_2S	This is a linear model compound containing only a sulfide function.
Pr_2SO	Sulfoxides are the first oxidation products of sulfides. If polymerization occurs in the presence of oxygen the sulfoxides formed may influence the course of reaction.
DBTP	Dilauryl ester is a known thermo-oxidative stabilizer. Due to its limited solubility in the monomers investigated, dibutyl ester having good solubility was synthesized as a representative of commercial stabilizers.
TMT and TPT	These cyclic dithioacetals contain readily abstractable hydrogen atoms and strongly influence photopolymerization of dimethacrylates initiated by benzophenone[13].
TMTPT	This contains no α-hydrogens with respect to the sulfide group.

The measurements were conducted at 40°C and 80°C in air or Ar. The initiation was performed by BCH and its concentration was kept at 0.04 M (40°C and 80°C, air), 0.002 M (40°C, Ar) and 0.001 M (80°C, Ar) for BDDA and 0.02 M (40°C and 80°C, air) for HDDA. The additive concentration was 0.25 M for Pr_2S, Pr_2SO, DBTP and TMT and 0.04 M for TMT, TPT, TMTPT and DMAE. These concentrations were chosen high enough to obtain easily visible changes during polymerization but sufficiently low to disregard dilution effects.

Let us consider first the course of polymerization of BDDA at 40°C in air. Under these conditions we have to take into account the known inhibitory effect of oxygen which leads to a reduction of the reaction rate and yield[19,20]:

$$R^{\bullet}+O_2\rightarrow ROO^{\bullet} \qquad (1)$$

The kinetic curves of the polymerization of formulations containing linear sulfides or cyclic dithioacetals and the reference curve obtained in the absence of sulfides are shown at *Figures 1* and *2*. Pr_2S and DBTP at a concentration of 0.25 M markedly enhance the polymerization rate and yield (by about 15–20%), and a somewhat better result was obtained in the case of DBTP (*Figure 1*). The influence of cyclic dithioacetals is much greater (*Figure 2*). In the presence of 0.25 M TMT the polymer yield exceeds 90%. When the TMT concentration was decreased sixfold to 0.04 M, the final monomer conversion remained unchanged although it was reached at a slightly lower rate. The kinetic curve for a formulation containing 0.04 M of an aliphatic amine-DMAE, the known oxidizable compound often

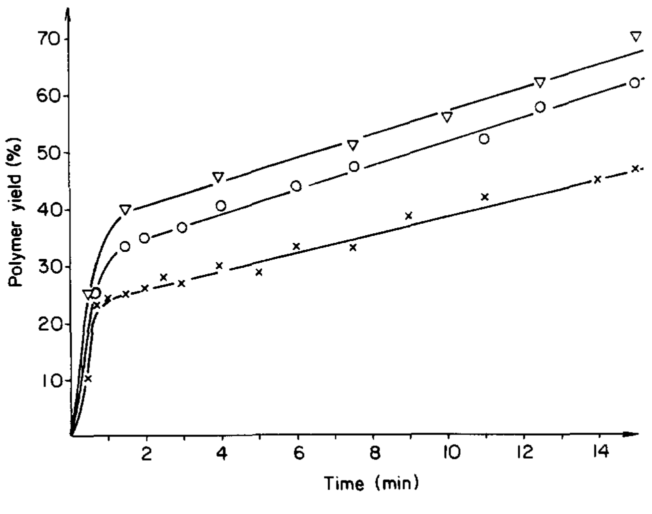


Figure 1 Kinetic curves of BDDA polymerization at 40°C in air in the presence of linear sulfides. Initiator: 0.04 M BCH. (×) Without additive; (○) in the presence of 0.25 M Pr_2S; (▽) in the presence of 0.25 M DBTP; (▼) in the presence of 0.25 M Pr_2SO; (△) in the presence of 0.25 M TMT; (▲) in the presence of 0.04 M TMT; (□) in the presence of 0.04 M TPT; (■) in the presence of 0.04 M TMTPT; (●) in the presence of 0.04 M DMAE

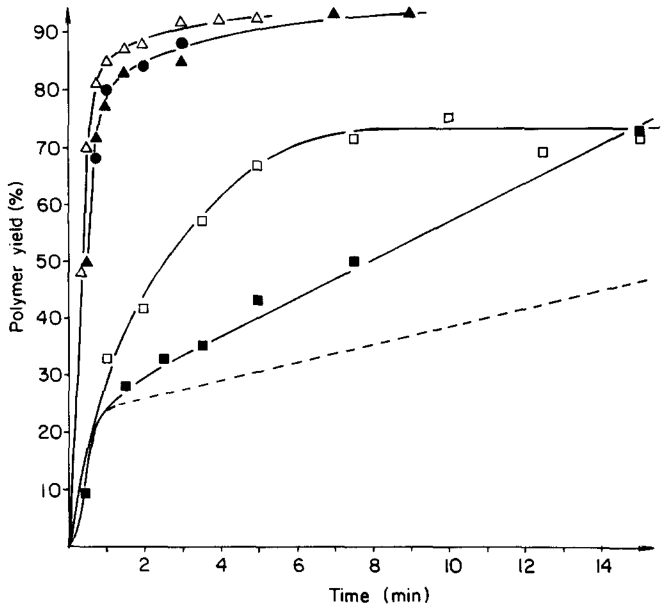


Figure 2 Kinetic curves of BDDA polymerization at 40°C in air in the presence of cyclic dithioacetals. Initiator: 0.04 M BCH. The dotted line represents polymerization without additive. Symbols as in *Figure 1*

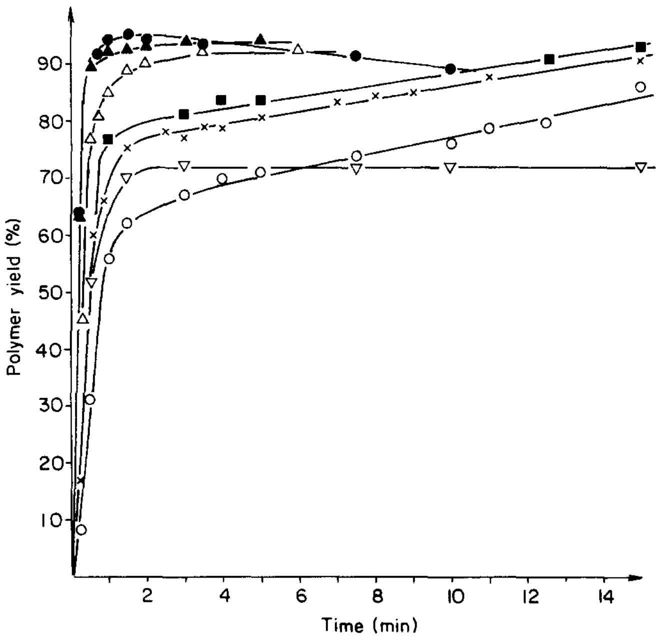


Figure 3 Kinetic curves of BDDA polymerization at 80°C in air. Initiator: 0.04 M BCH. Symbols as in *Figure 1*

used to overcome oxygen inhibition, almost coincides with the kinetic curve obtained for 0.04 M TMT. This proves that the ability of these two compounds to scavenge oxygen is similar under the conditions used.

The influence of cyclic dithioacetals having phenyl substituents, i.e. TPT and TMTPT, is not as great as that of TMT, although the increase in polymer yield is high.

Different results were obtained at 80°C. The use of a higher temperature was imposed by the fact that u.v. light sources used in commercial curing processes generate a large amount of heat which raises the polymerization temperature. The results are given in *Figure 3*. The curves presented were obtained under the same conditions (except temperature) as those in *Figures 1* and *2*. The basic difference observed is that at 80°C linear sulfides exert a retarding rather than an accelerating effect, which appears at 40°C. In contrast, the addition of cyclic dithioacetals to a formulation enhances the rate and yield of the reaction at 80°C.

The influence of 0.04 M DMAE up to about 2 min for the reaction at 80°C is similar to that of 0.04 M TMT, but after this period the yield of the amine-containing polymer begins to drop, indicating destruction of the product; this destruction was not observed in the presence of cyclic dithioacetals.

The change in the action of linear sulfides from an enhancing rate and yield at 40°C to reducing them at 80°C suggests that there exists a temperature at which these two effects are compensated and the kinetic curves of the sulfide-containing and the sulfide-free formulation are similar. Indeed, this was observed at 60°C for Pr_2S.

To find whether the influence of aliphatic sulfides on the polymerization process conducted in air is connected with the action of oxidation products of sulfides, kinetic curves of the reaction carried out in the presence of Pr_2SO were obtained. It was found that the sulfoxide practically does not affect polymerization at both 40°C and 80°C. Therefore we can conclude that, although linear sulfides partly remove the inhibitory effect of oxygen at moderate temperatures, this is not connected with the radical processes occurring in the later oxidation stages of the sulfides, which was suggested earlier[13,21]. The action of the sulfides is based on their own properties, in particular their hydrogen donor ability.

A second set of experiments was carried out in an inert atmosphere. At 40°C both Pr_2S and DBTP slightly reduce the rate and yield of the polymerization (*Figure 4*). A somewhat larger decrease in the reaction yield is caused by Pr_2S at 80°C (*Figure 5*). In contrast to the results obtained in air-saturated systems, at 40°C in Ar cyclic dithioacetals markedly reduce both the rate and yield of the polymerization (*Figure 6*) and this effect depends strongly on their structure; the greatest effect is produced by TPT.

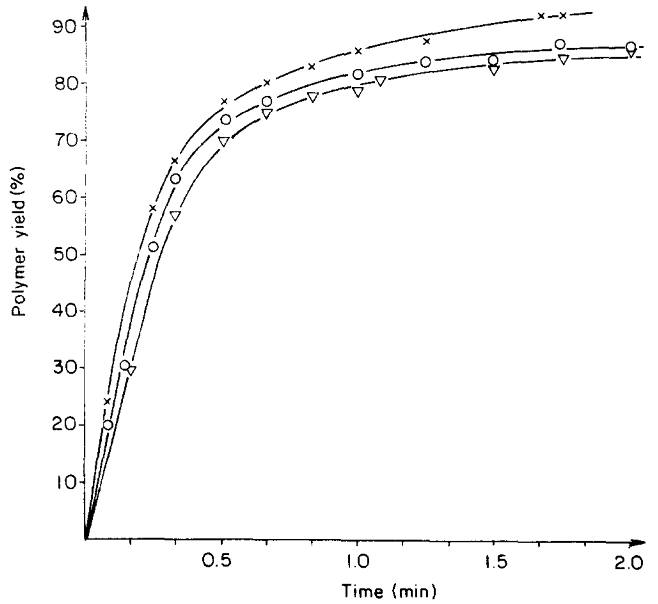


Figure 4 Kinetic curves of BDDA polymerization at 40°C in Ar in the presence of linear sulfides. Initiator: 0.002 M BCH. Symbols as in *Figure 1*

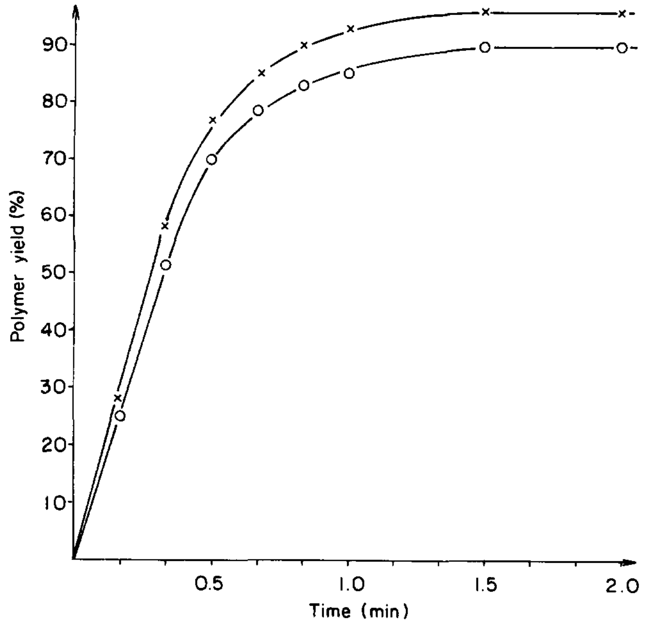


Figure 5 Kinetic curves of BDDA polymerization at 80°C in Ar in the presence of Pr_2S. Initiator: 0.001 M BCH. Symbols as in *Figure 1*

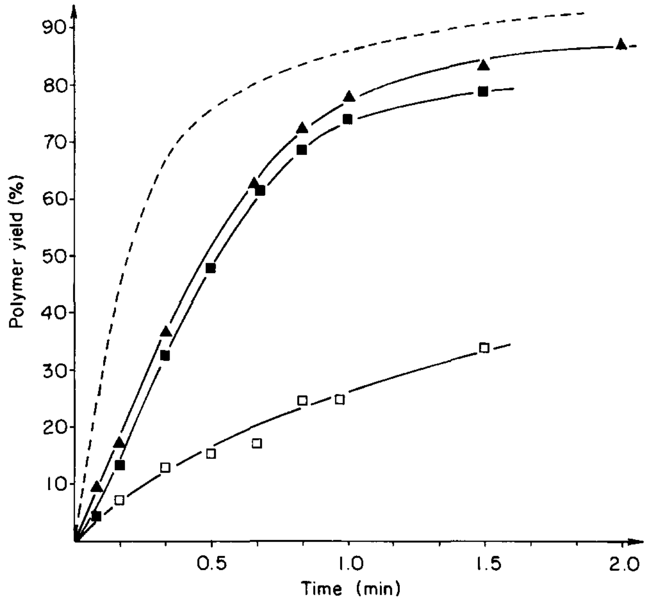


Figure 6 Kinetic curves of BDDA polymerization at 40°C in Ar in the presence of cyclic dithioacetals. Initiator: 0.002 M BCH. The dotted line represents polymerization without additive. Symbols as in *Figure 1*

There exists a possibility that during the illumination of a sulfide-containing formulation direct photolysis of the sulfide occurs, caused by its residual absorption in the irradiation region. The radicals thus produced may influence the course of polymerization. The experiments carried out in Ar at 40°C in the absence of any photoinitiator indicate the formation of radicals able to initiate polymerization under these conditions from both the sulfides and sulfoxide (*Figure 7*). The most effective initiation occurs in the case of Pr_2SO when about 55% of monomer conversion was obtained. Somewhat less effective in initiation was Pr_2S, whereas the photolysis of cyclic dithioacetals led to only small amounts of the polymer, and this may be indicative of the low reactivity of the derived radicals. However, the effectiveness of radical formation during photolysis of the additives used is low since polymerization is completely suppressed in the presence of atmospheric oxygen. Therefore the photolysis of the additives should not play an important role in the initiation of polymerization, especially in the presence of an effective source of radicals, but may be helpful in overcoming oxygen inhibition.

The results presented above refer to the polymerization of BDDA. The polymerization of the more often used monomer, HDDA, was found to be less sensitive to the action of sulfides (*Figures 8* and *9*). Addition of Pr_2S mainly affects the polymerization rate at 40°C and 80°C, the limiting conversion being unchanged. DMAE and TMT enhance both the rate and yield.

The swelling measurements of the polymerization products of the sulfide-containing and sulfide-free formulations were performed in water and xylene (*Table 1*). Although water swelling is very low, it is clearly seen that polymers containing bound-in Pr_2S are 50% less swellable in H_2O. This is very important from the point of view of practical applications when high hydrophobic properties of the product are needed. The greater swelling of the sulfide-containing polymers in xylene indicate, in turn, that the crosslink density of these polymers is reduced and/or that the presence of Pr_2S enhances xylene compatibility with poly(diacrylates).

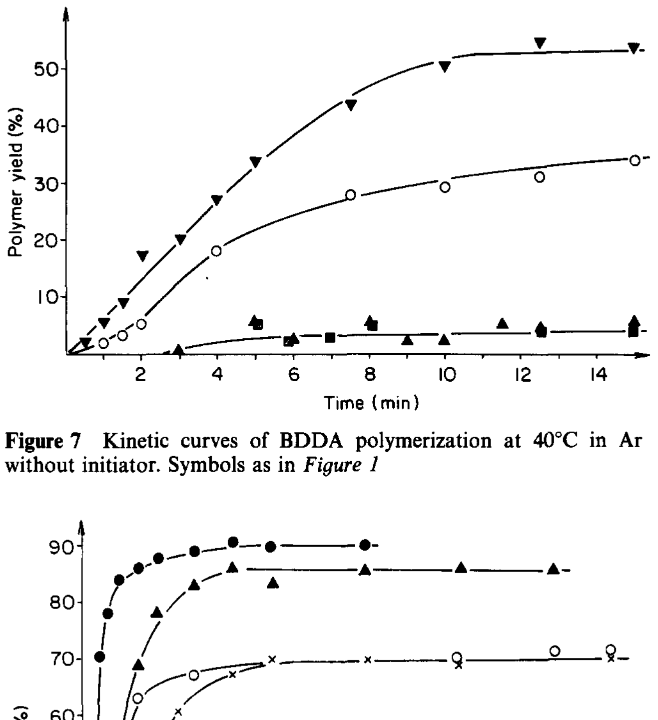


Figure 7 Kinetic curves of BDDA polymerization at 40°C in Ar without initiator. Symbols as in *Figure 1*

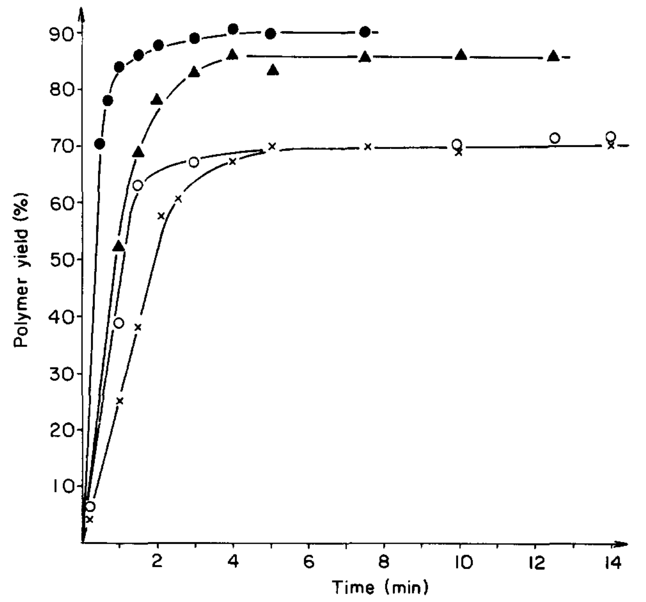


Figure 8 Kinetic curves of HDDA polymerization at 40°C in air. Initiator: 0.02 M BCH. Symbols as in *Figure 1*

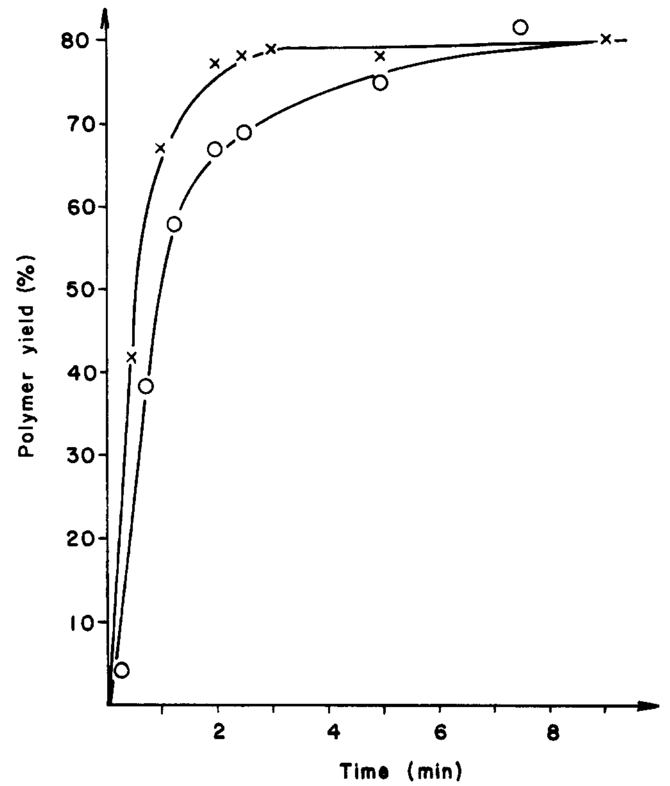


Figure 9 Kinetic curves of HDDA polymerization at 80°C in air. Initiator: 0.02 M BCH. Symbols as in *Figure 1*

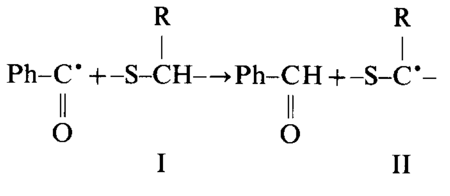
Table 1 Swelling of polymers (wt%)

Polymer sample	Water after 72 h	Xylene after 144 h
Poly-HDDA	0.4	9.0
Poly-HDDA containing Pr_2S	0.2	9.3
Poly-BDDA	0.9	2.3
Poly-BDDA containing Pr_2S	0.5	2.8

As shown in the literature, aliphatic sulfides possess a good hydrogen-donor ability, whereas the derived sulfoxides are rather poor hydrogen donors[22]. The fact that sulfoxides practically do not affect the course of polymerization suggests that hydrogen abstraction is the most important reaction in the mechanism influencing sulfides on the polymerization of diacrylates.

During the polymerization of a formulation containing a sulfide additive the following hydrogen abstraction reactions can take place:

1. By the photoinitiator-derived radical:



$$\underset{\text{I}}{\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}^{\bullet}}} + \mathrm{{-}S{-}\overset{\overset{R}{|}}{C}H{-}} \rightarrow \mathrm{Ph{-}\underset{\underset{O}{\|}}{C}H} + \underset{\text{II}}{\mathrm{{-}S{-}\overset{\overset{R}{|}}{C}^{\bullet}{-}}} \qquad (2)$$

Such reactions of benzoyl radicals are possible with hydrogen donors and play a role in the polymerization process[23].

2. By a macroradical (chain-transfer reaction):

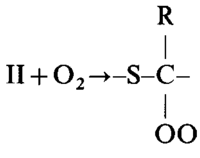
$$\sim\!\!\sim M^{\bullet} + \text{I} \rightarrow \sim\!\!\sim MH + \text{II} \qquad (3)$$

This reaction reduces the crosslink density.

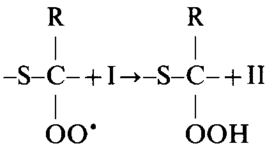
3. By peroxy radicals (chain-peroxidation process): either formed by oxygen addition to the macroradical or the initiator-derived radical (see reaction (1)):

$$ROO^{\bullet} + \text{I} \rightarrow ROOH + \text{II} \qquad (4)$$

or formed by oxygen addition to radical II:



$$\text{II} + O_2 \rightarrow \mathrm{{-}S{-}\overset{\overset{R}{|}}{\underset{\underset{OO^{\bullet}}{|}}{C}}{-}} \qquad (5)$$



$$\mathrm{{-}S{-}\overset{\overset{R}{|}}{\underset{\underset{OO^{\bullet}}{|}}{C}}{-}} + \text{I} \rightarrow \mathrm{{-}S{-}\overset{\overset{R}{|}}{\underset{\underset{OOH}{|}}{C}}{-}} + \text{II} \qquad (6)$$

The formation of the polymer during the irradiation of the monomer plus additive mixture in the absence of initiator suggests that in addition to the hydrogen abstraction reaction photolysis of the additive also occurs:

$$R{-}S{-}R' \xrightarrow{h\nu} R{-}S^{\bullet} + R'^{\bullet} \qquad (7)$$

$$R{-}SO{-}R' \xrightarrow{h\nu} R{-}SO^{\bullet} + R'^{\bullet} \qquad (8)$$

Reactions (7) and (8) show only the primary processes; the further photolysis of dithioacetals depends strongly on the reaction atmosphere[24].

Taking into account that, during photopolymerization, reactions (2), (3), (7) and (8) (in an inert atmosphere) or (2)–(8) (in air) are possible we will attempt to explain the results obtained.

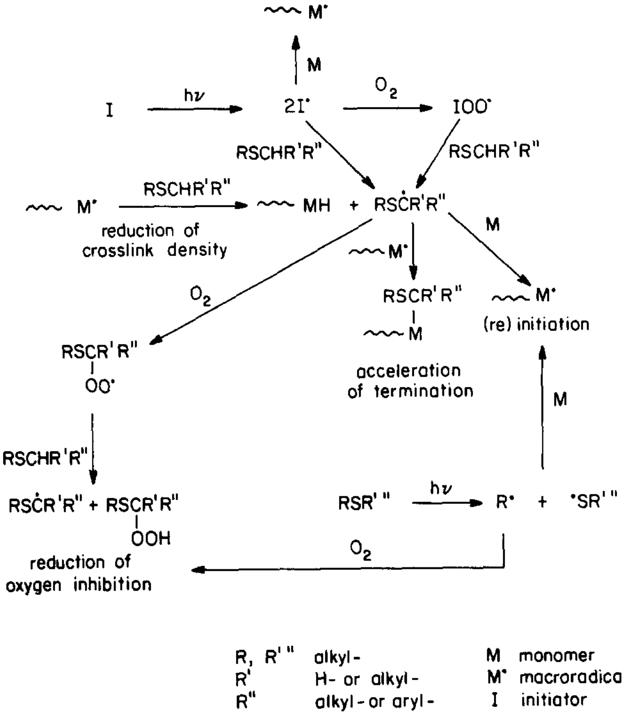
The slightly retarding action of sulfides in an argon atmosphere may be connected with the chain-transfer on the additive (reaction (3)), which in turn may retard polymerization as a result of two processes: acceleration of termination by the introduction of a certain mobility of the radical sites in the vitrifying medium[8]; slow reinitiation process (which has also been found for amines[25,26]):

$$\text{II} + M \rightarrow \sim\!\!\sim M^{\bullet} \qquad (9)$$

where M = monomer molecule.

The rates of these processes depend on the hydrogen-donor ability of the additive used and on the reactivity of the derived radical, therefore the retarding effect of linear sulfides is less pronounced than that of cyclic dithioacetals having readily abstractable hydrogens and more stabilized radicals II (by two S atoms[22]). The greatest effect caused by TPT may be attributed to the low reactivity of its highly stabilized radical II in reaction (9) and, as a result, its enhanced participation in chain termination (the more so as TPT-derived radicals II, in contrast to TMT• radicals, remain unaffected by 366 nm light[13]). On the other hand, TMTPT, having no mobile hydrogens, acts similarly to TMT, indicating that other retarding reactions probably caused by the photolysis products of TMTPT also take place.

At 80°C an additional acceleration of termination occurs caused by the fact that the activation energy of the chain-transfer reaction is higher than the activation



Scheme 1 Effect of aliphatic sulfides on the polymerization of multi(meth)acrylates

energy of propagation[11]. This supposition is confirmed by a larger decrease of the polymer yield in the presence of Pr_2S in Ar at 80°C than at 40°C.

In the presence of atmospheric oxygen the situation presented above changes completely due to the occurrence of reactions (4)–(6). Because at 40°C all the investigated additives enhance the rate and yield of the polymerization, it is evident that the most important process is chain-peroxidation, leading to enhanced oxygen consumption (reactions (5) and (6)). The rates of these reactions also depend on the hydrogen-donor ability of the additive, therefore the greatest effects are observed for TMT and TPT. This means that at 40°C reactions (5) and (6) are much faster than the retarding processes described above.

It is interesting that, at 80°C in air, linear sulfides and cyclic dithioacetals affect polymerization in a different way. We can assume that at this temperature the slowing-down processes described above become faster than oxygen consumption caused by linear sulfides, the more so as oxygen solubility markedly drops in comparison with a temperature of 40°C. Therefore, at a temperature of about 60°C the rate of oxygen consumption (reactions (5) and (6)) would be the same as the increase in the termination rate caused by Pr_2S.

The fact that at 80°C both TMT and DMAE (good hydrogen donors) still accelerate the polymerization process whereas the influence of TMTPT is low suggests that this phenomenon is also connected more with the hydrogen abstraction reaction and oxygen scavenging than with specific photolysis reactions of dithioacetals. It is possible that in this case the rates of reactions (5) and (6) are still high enough to counteract the detrimental effect of acceleration in termination caused by the rise in temperature. However, the chain-transfer reaction at 80°C competes to a higher degree than at 40°C with reactions (5) and (6) since the increase in TMT concentration from 0.04 to 0.25 M slightly reduces the polymerization rate at 80°C, whereas the same change of TMT concentration at 40°C accelerates the reaction (*Figures 2* and *3*).

In conclusion, we can say that the observed effect of sulfide action on polymerization is a result of retarding and accelerating processes occurring simultaneously and their relationship depends on the reaction conditions and the sulfide structure.

The most important reactions of sulfides which can take place during photopolymerization of diacrylates are summarized in *Scheme 1*.

A similar influence of sulfides, although less pronounced, was observed for the polymerization of 1,4-butanediol dimethacrylate initiated by α,α-dimethoxy-α-phenylacetophenone[27]. Therefore we believe that *Scheme 1* should also be valid for multi(meth)acrylates and, to a greater extent (reduction of crosslink density should be replaced by reduction of molecular weight), for mono(meth)acrylates.

However, care must be taken when considering di(meth)acrylate monomers containing the thioether linkage inside the ester group. In this case an enhancement of the crosslink density will occur and also such factors as the improved flexibility of the chain connecting the two unsaturations[14], and the lower reactivity of the sulfur-containing macroradical[28] may affect the course of polymerization.

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