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Effect of the sulfide group on photopolymerization kinetics of di(meth)acrylates

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Summary

The photopolymerization of four analogous monomers: 2,2'-thiobisethanol diacrylate and its dimethacrylate plus 2,2'-oxybisethanol diacrylate and its dimethacrylate has been studied by isothermal differential scanning calorimetry (DSC) over a range of incident light intensities. The results obtained prove that the sulfide group accelerates polymerization both in the presence and absence of oxygen and enhances the conversion. The light intensity exponents for each monomer were determined and the mechanism of termination was discussed. The intensity exponents of sulfur-containing monomers are lower than their corresponding oxygen analogues, pointing to a greater participation of the bimolecular termination during their polymerization.

Introduction

The introduction of a sulfide group into the ester group of aliphatic diacrylates and dimethacrylates is advantageous both for their photopolymerization (1-3) and for the polymer properties (improved thermooxidative stability (4), reduced moisture absorption (2, 5), higher refractive index (1)).

The beneficial effect of the thioether bond is associated mainly with the enhanced hydrogen abstraction from the CH_2 group attached to the sulfur atom. This reaction increases network crosslink density by grafting and influences mobility of radical sites affecting the termination and reinitiation processes. In air it accelerates oxygen consumption leading to reduction of oxygen inhibition. The importance and in turn, the influence of each of these processes, changes with temperature (1-3).

Another important external factor affecting the photopolymerization, beside temperature, is the incident light intensity. Usually, both the reaction rate and monomer conversion increase with the radiation intensity. The light intensity exponent may indicate the way in which termination of the polymerization occurs.

If the intensity exponent is equal to 0.5, bimolecular (second order) termination takes place, which results from the known equation on the photopolymerization rate (6):

$$\mathbf{R_p = k_p / (k_t^b)^{0.5} \bullet [M] \bullet [\Phi \bullet I_0 \bullet (1 - e^{-\varepsilon[A]l})]^{0.5}} \qquad (1)$$

where k_p and k_t^b are propagation and bimolecular termination rate constants, resp., Φ is quantum yield of initiation, I_0 is incident light intensity, [M] is concentration of double bonds, ε is extinction coefficient, [A] is photoinitiator concentration and l is layer thickness.

The light intensity exponent may deviate from the value of 0.5, both towards unity and towards zero. It may change with conversion: both an increase of the exponent with conversion above the value of 0.5 (7-9) as well as a decrease below this value (10) was reported. The deviation towards unity is usually associated with a tendency to first order or pseudo-first order termination, when the radicals do not recombine or under certain conditions of inhibition (6). A deviation of the exponent towards zero may indicate on high contribution of primary termination caused by recombination with initiator derived (primary) radicals. This may be observed when primary radicals are produced at too high a concentration (which is likely to occur at high light intensities) and/or in the presence of too low a monomer concentration to be completely and rapidly scavenged by the monomer. Under conditions where bimolecular termination between propagating radicals becomes difficult (due to increased viscosity, heterogeneity or radical trapping), primary termination may become important or even the only mode of termination. The latter leads to zero order in I_0 (6).

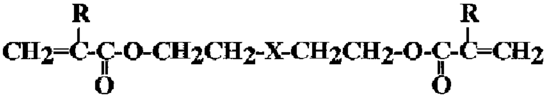
In practice, all the termination pathways described above may take place simultaneously: first order and pseudo-first order reaction, second order reaction and reaction with primary radicals. Timpe *et al.* (10,11) proposed a semi-empirical equation for describing the polymerization process, especially in viscous media:

$$\mathbf{R_p = k(x) \bullet (1\text{-}x)^{\alpha} \bullet I_0^{\beta}} \qquad (2)$$

where x is the conversion of double bonds (expressed as a fraction), k(x) is a conversion dependent quantity, I_0 is the incident light intensity (in mW/cm^2) and α and β are exponents; R_p is expressed in s^{-1}.

The value of β exponent should indicate the termination mechanism: $\beta = 1$ - first order termination, $\beta = 0.5$ to 1 - combined first and second order termination, $\beta = 0.5$ - second order termination, $\beta < 0.5$ - combined second order and primary radical termination.

The aim of the present work was to find how the sulfide group, introduced to the monomer molecule, affects the polymerization course and termination process of both diacrylates and dimethacrylates at various incident light intensities. For this purpose the polymerization of sulfur-containing monomers was compared to that of their oxygen analogues. The following compounds were investigated: 2,2'-thiobisethanol diacrylate (TEDA), 2,2'-thiobisethanol dimethacrylate (TEDM), 2,2'-oxybisethanol diacrylate (OEDA) and 2,2'-oxybisethanol dimethacrylate (OEDM).



$$CH_2{=}\overset{R}{\overset{|}{C}}{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2CH_2{-}X{-}CH_2CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}\overset{R}{\overset{|}{C}}{=}CH_2$$

	R = H	**R = CH_3**
X = S:	**TEDA**	**TEDM**
X = O:	**OEDA**	**OEDM**

The work is part of a continuing investigation of the influence of the sulfide group on the polymerization of multiacrylates (1-3, 5, 12-14).

Experimental

The monomers were synthesized in the reaction of appropriate glycols (Merck, Darmstadt) with acroyl chloride or methacroyl chloride (Merck) in the presence of triethylamine (Merck) in a dichlormethane solution according to a procedure described elsewhere (2).

The polymerization kinetics were monitored under isothermal conditions at 40 ± 0.01°C by a differential scanning calorimeter (DSC 605 M, UNIPAN-TERMAL, Warsaw, Poland) equipped with a lid specially designed for photochemical measurements. The reaction was initiated with the 366 nm light and 0.02 M (~ 0.5 wt %) α,α-dimethoxy-α-phenylacetophenone (Irgacure 651 from Ciba-Geigy). The procedure was the same as given in reference 2. When the polymerization was carried out in an inert atmosphere, the sample was equilibrated in the apparatus under argon (0.0005% O_2) for 10 minutes. The incident light intensity (measured by the carbon black method which gave an accurate value at the sample position) changed in the range of about 1 - 3.5 mW/cm^2. PET filters were used to vary the light intensity. Repeated DSC runs were identical in shape and yielded consistent polymerization rates (error at peak maximum ≤ 3%). The final conversion was also quite reproducible, with an error not more than ± 3%. For calculations the polymerization heats 86 kJ/mol for acrylates (2) and 56 kJ/mol for methacrylates (6) were taken. The final conversion was determined as the conversion at the time at which the polymerization rate decreased to 0. The obtained DSC data were analyzed for the corrected baseline.

Results and discussion

The results presented in this work enable direct comparison of the reactivity of the investigated acrylates and methacrylates under conditions of oxygen inhibition over a range of incident light intensities. The influence of light intensity on polymerization in the absence of oxygen was observed for two dimethacrylates: TEDM and OEDM.

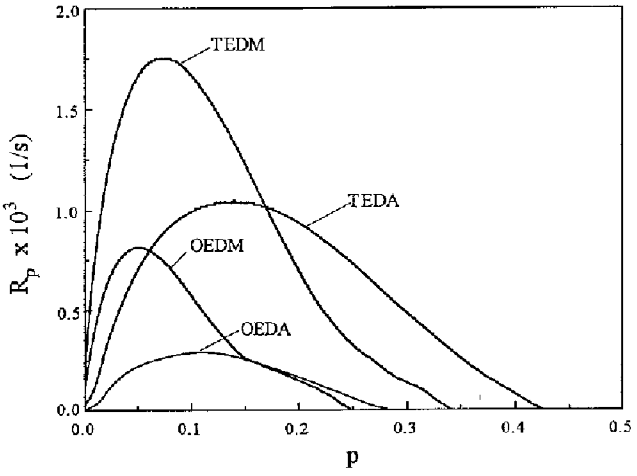


Fig. 1. Polymerization rates (R_p) in air at I_0 = 1.5 mW/cm^2 as a function of double bond conversion (p).

The effect of the sulfide group on the course of polymerization

Figure 1 shows the conversion degree - polymerization rate curves for all the monomers in air at an incident light intensity $I_0 = 1.5$ mW/cm^2. As can be seen, the sulfur-containing monomers polymerize much faster and to higher conversions than their oxygen analogues. This effect is observed in the whole intensity range studied and although is high for both acrylates and methacrylates, it is more pronounced for acrylates.

The most important parameters which characterize the autoacceleration and thus the course of the polymerization, are: final conversion p^f, rate at peak exotherm (maximum polymerization rate R_p^{max}), time required for R_p^{max} and conversion at R_p^{max} (p_{Rm}).

Although the extent of conversion of acrylates usually exceeds those of corresponding methacrylates, the beneficial influence of the sulfide group (resulting from the reduction of oxygen inhibition) makes the final conversion of TEDM higher that of OEDA at all light intensities used (Fig. 2a) and p^f values in air decrease in the following order of monomers:

TEDA > TEDM > OEDA > OEDM.

As expected, the final conversion increases with the light intensity due to two effects: i). growing contribution of oxygen consumption, both dissolved and diffusing, by initiator radicals and ii). increasing reaction rate which leads to enhanced conversion due to delayed shrinkage (15). The first effect seems to be more important under the conditions used in this work, since p^f of the monomers polymerized in Ar atmosphere increases only slightly with I_0 (Fig. 2a). Somewhat higher p^f values of TEDM that those of OEDM in Ar may result from better network mobility of the polymer (16) due to the lower barrier to rotation of the C-S bond (1-3).

The sulfide group also significantly reduces the time required for R_p^{max}, especially in air (about three times in the case of acrylates). This effect is stronger for acrylates which are more susceptible to oxygen inhibition (17).

The dependence of the conversion at R_p^{max} on I_0 is shown in Fig. 2b. In air the order of monomers with decreasing tendency of p_{Rm} is as follows (compare also Fig. 1):

TEDA > OEDA > TEDM > OEDM.

The lower p_{Rm} values for methacrylates result from the fact that the decelerating processes during their polymerization set in earlier than in the polymerization of acrylates (3) and the better position of the sulfur-containing monomers is caused, as discussed above, by faster oxygen consumption by these compounds. In the absence of air, p_{Rm} values of TEDM are lower than corresponding values of OEDM due to faster a chain transfer reaction in the presence of the sulfide group. The resulting grafting leads to earlier gelation and appearance of R_p^{max} at lower conversions.

The conversion at which the maximum rate occurs is known to increase with the light intensity due to delay in volume shrinkage mentioned above. The practically constant p_{Rm} value of TEDM in Ar over the whole intensity range may suggest that the relaxation of its polymer network is very fast near R_p^{max} so that equilibrium is maintained (18). Since this effect is not observed in OEDM polymerization we may suppose that it results from better flexibility of the poly-TEDM network. In air p_{Rm} values increase with light intensity due to the same reasons as do p^f values.

The dependence of the maximum polymerization rate on I_0 is given in Fig. 2c. The arrangement of monomers according to decreasing R_p^{max} values in air is as follows:

TEDM > TEDA > OEDM > OEDA.

The observed order results from two factors: i). lower sensitivity of the polymerization rate of methacrylates to oxygen inhibition and ii). reduction of the oxygen effect by the sulfide group. However, at lower conversion degrees the methacrylates polymerize faster

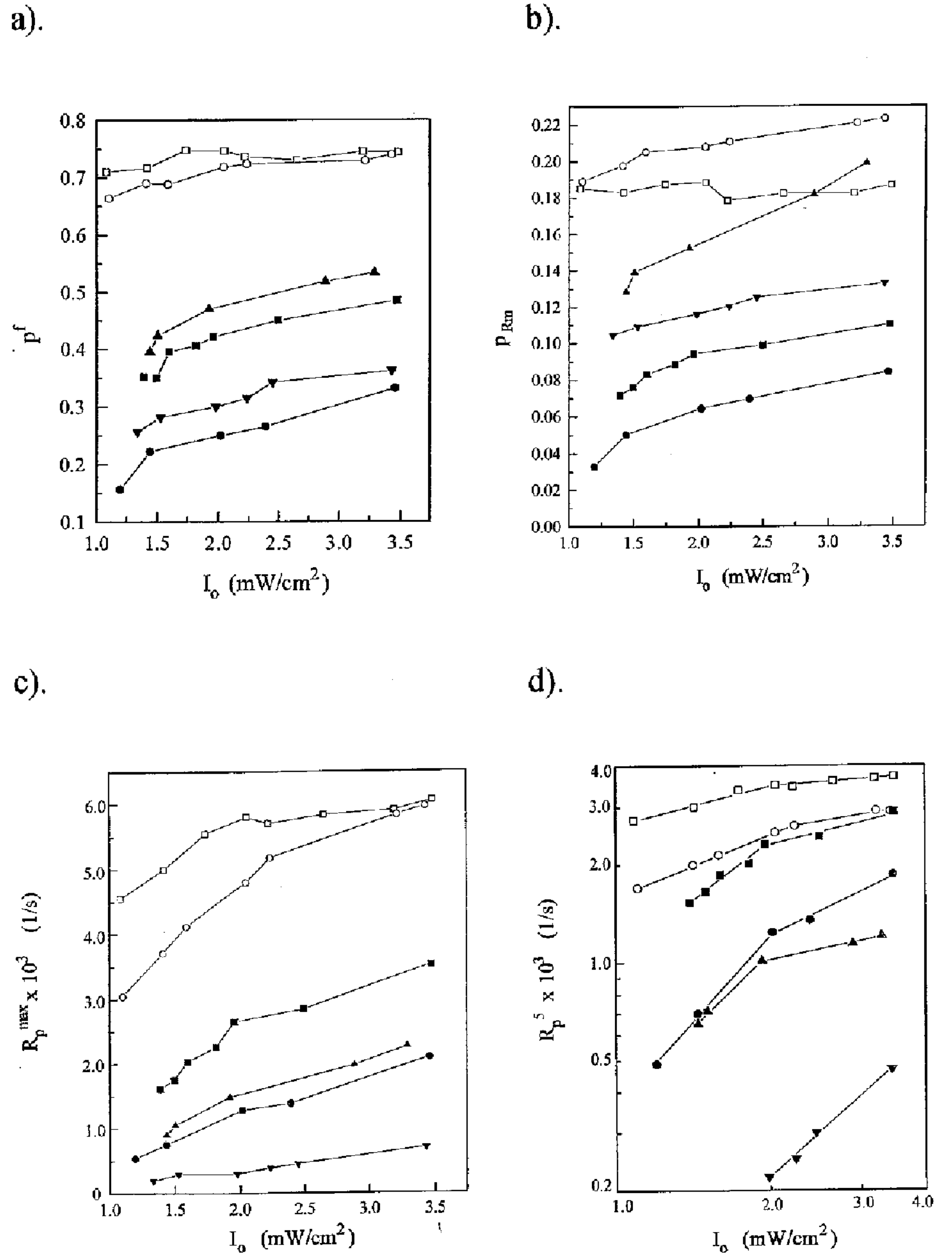


Fig. 2. a). Final conversion, b). double bond conversion at maximum polymerization rate, c).maximum polymerization rate and d). polymerization rate at p=0.05, as a function of incident light intensity. Open symbols denote polymerization in Ar atmosphere, filled symbols denote polymerization in air.

□,■ -TEDM, ○,● - OEDM, ▲- TEDA, ▼- OEDA.

than the acrylates (Figs. 1 and 2d) which suggests that the first factor is more important in determining the polymerization rates at the beginning of the reaction.

In Ar the sulfur-containing monomer shows higher R_p^{max} values than its oxygen analogue which must result from other effects than faster oxygen consumption by the $-CH_2S-$ group. The difference is well-marked at lower intensities and decreases with increasing I_0 until R_p^{max} of OEDM approaches R_p^{max} of TEDM at the highest light intensities. This is clearly indicated with the difference in the light intensity exponents of these two monomers.

Light intensity exponents

The light intensity exponents were calculated according to equation (2) from the log-log dependence of R_p on I_0 for a chosen conversion degree (in this case two other quantities in the equation (2) become constant).

The obtained log-log plots are linear with a change in the slope at about 2 mW/cm^2 (see Fig. 2d as an example). This gives two β values for each R_p on I_0 dependence: the higher β for the lower intensity region (< 2 mW/cm^2) and the lower β for the higher intensity region (> 2 mW/cm^2). The β values were calculated for various degrees of conversion and are summarized in Tables 1 and 2. The β exponent for OEDA polymerization in air in the lower intensity region was not determined due to the very low R_p values and hence possible higher measurement error.

The change of the β exponent near 2 mW/cm^2 is probably not sharp but reflects the changes which occur in the termination process with increasing light intensity and hence increasing initiation rate.

Analyzing the β exponents obtained for the polymerization of dimethacrylates under conditions unperturbed with oxygen influence (Table 1) we observe that in the whole intensity range for OEDM and in the lower intensity region for TEDM the β exponent shows the often observed behaviour - an increase with conversion. In the

Table 1. Intensity exponents at various conversion degrees for polymerization in Ar.

Monomer	I_0 range mW/cm^2	β			
		p = 0.05	p = 0.20	p = 0.45	p = 0.60
TEDM	<2	0.40	0.41	0.64	1.21
	>2	0.13	0.09	0.09	0.04
OEDM	<2	0.68	0.70	1.01	1.55
	>2	0.28	0.32	0.5	0.85

Table 2. Intensity exponents at various conversion degrees for polymerization in air.

Monomer	I_0 range mW/cm^2	β				
		p = 0.05	p = 0.10	p = 0.15	p = 0.20	p = 0.30
TEDM	<2	1.14	1.59	2.19	3.19	3.92
	>2	0.41	0.49	0.63	0.83	1.54
TEDA	<2	1.59	1.77	2.09	2.37	3.23
	>2	0.32	0.53	0.7	0.93	1.38
OEDM	<2	1.71	3.31	5.49		
	>2	0.77	1.18	1.81	3.01	
OEDA	>2	1.29	1.49	1.59	1.87	

absence of oxygen the monomolecular termination results from the radical trapping in the polymer network. As the reaction progresses, the network densifies and the radical trapping increases, enhancing the β value. In the lower intensity region the β exponents for TEDM up to middle conversions are somewhat lower than 0.5 suggesting that bimolecular termination dominates and may be accompanied by primary termination. However, the contribution of the monomolecular reaction to the overall termination process increases with conversion, enhancing β to a value even higher than 1. The intensity exponent of OEDM starts in turn from a value higher than 0.5 at a low degree of conversion and monotonically increases pointing to the participation of monomolecular termination from the early polymerization stages and its domination at larger extents of conversion.

The β exponents of both monomers above 2 mW/cm^2 and at $p = 0.05$ are surprisingly low. Cook (9) reported the β exponents for OEDM at various degrees of conversion to be close to those found in this work. He explained the anomalously low intensity exponent at high initiation rates (high radiation intensities) in light of the reduced kinetic chain length. Since the rate-determining termination mechanism in the autoacceleration regime is chain length dependent translational diffusion, the termination rate at high radiation intensities will be faster than otherwise expected and will moderate the increase in polymerization rate with light intensity. At higher conversions (near R_p^{max}) the mechanism of reaction diffusion, which is insensitive to kinetic chain length, starts to dominate and the anomalously low radiation exponent should rise. This may in part explain the very low initial β exponents of OEDM and TEDM polymerizations in the higher intensity region. However, TEDM polymerization shows an exceptional behaviour: its intensity exponent drops with increasing conversion. Similar results were obtained for photopolymerization in polymeric binders (10). They were explained by the fact, that at high conversion levels diffusion of macroradicals is restricted in the vitrifying medium but small initiator radicals are still able to diffuse leading to domination of primary termination. Because this effect is not observed in OEDM polymerization, at the present it is difficult to explain the reason for extremely low β values of TEDM above 2 mW/cm^2.

The calculated β values are resultants from various termination ways and for instance, $\beta = 0.5$ (as found in the case of OEDM at $p = 0.45$) may not mean a pure bimolecular reaction but a mixture of the monomolecular reaction (which increases β) and the bimolecular reaction with corresponding β value lowered by the participation of primary termination.

In the presence of air the polymerization is strongly retarded and pseudo-first order reaction with oxygen becomes the important way of termination. As a result, the values of the β exponents should significantly rise (Table 2). In the lower intensity region the β exponents in all cases markedly exceed the value of 1 and increase with conversion. This suggests that: i). the main termination ways are probably first order and pseudo-first order reactions and ii). the intensity exponent reflects not only the chemical type of termination mechanism but also such factors as diffusion effects on the polymerization rate in viscous media and the relationship between the polymerization rate and rates of oxygen diffusion and consumption. These factors may increase the β exponent to a value higher than theoretically possible. Kloosterboer (18) found for 1,6-hexanediol diacrylate at $p = 0.3$ and at a low intensity radiation, the intensity exponent equal to 2 in the presence of only 58 ppm of oxygen, whereas in the presence of 2 ppm of oxygen the intensity exponent dropped to 0.7. He concluded that oxygen strongly influences the kinetics of network formation.

In the higher intensity region, the rate of radical formation and hence the rate of oxygen consumption, becomes so fast that the effect of oxygen is reduced. The β exponents decrease at low conversions to values <1 indicating that in these cases first order, pseudo-first order and second order termination simultaneously may occur (the possibility of the primary termination may be partly eliminated by the reaction of initiator radicals with oxygen). Since during the polymerization of sulfur-containing monomers, oxygen is removed much faster than during the polymerization of corresponding oxygen analogues (1-3), the β exponents for TEDM and TEDA are less influenced by the pseudo-first order reaction.

Discussing the influence of the sulfide group on the polymerization of di(meth)acrylates, we can draw from Tables 1 and 2 the general conclusion that the polymerization of sulfur-containing monomers is characterized by lower intensity exponents, both in Ar and air. The lower β exponents for TEDM than those for OEDM observed in Ar, may point to a greater contribution of the bimolecular reaction to the overall termination process in TEDM polymerization. This result may be a consequence of the chain-transfer reaction, being faster for sulfur-containing monomers due to the better chain transfer activity of sulfides than ethers (1-3, 6). Chain transfer enhances the mobility of radical sites, especially trapped ones, enabling them to react with a monomer or another radical site.

In air, the lower β exponents for TEDM and TEDA polymerization result simultaneously from the partial elimination of the reaction of macroradicals with oxygen, and from the effect of chain transfer on the mobility of radical sites described above.

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