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Sulfur-containing polyacrylates: V. Temperature effects on the photoinitiated polymerization of diacrylates

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The influence of temperature on the photopolymerization kinetics of three analogous monomers, 2,2'-thiobisethanol diacrylate, 2,2'-oxybisethanol diacrylate and 1,5-pentanediol diacrylate, has been studied by isothermal differential scanning calorimetry in the temperature range of 30-100°C in air and in Ar atmosphere. The presence of the heteroatom markedly enhances the final conversion and maximum polymerization rate in air over the whole temperature range. This effect is much more pronounced for the sulfur-containing monomer. The final conversions of the monomers increase with temperature up to 100°C in air but in Ar they pass through a maximum at about 70°C in the case of monomers that do not contain sulfur. The sulfide group prevents the drop of cure extent in Ar at higher temperatures. The obtained results (kinetic parameters, activation energy) are discussed mainly in terms of hydrogen abstraction reaction.

(Keywords: diacrylates; sulfide group; temperature effects; photopolymerization)

INTRODUCTION

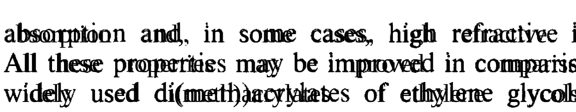
Photoinitiated free-radical polymerization of multifunctional monomers has found many industrial applications, especially in such areas as production of protective coatings, imaging systems and lithography[1,2]. The monomers that are most widely used for photopolymerization processes are diacrylates and dimethacrylates.

The kinetics of the photopolymerization of di(meth)acrylates of various types have been intensively studied (see, for example, refs 1, 3-5) and most often used methods are isothermal photocalorimetry[6] and real-time i.r. spectroscopy[7]. Fewer papers have been devoted to the temperature dependence of the polymerization course of multi(meth)acrylates. After the early work of Tryson and Schultz[8] concerning hexanediol diacrylate and pentaerythritol tetraacrylate, further studies dealt with the polymerization of acrylated urethanes[9], bisphenol A-based di(meth)acrylates[10,11] and recently oligo(ethylene oxide) and oligo(methylene oxide) dimethacrylates up to temperatures higher than 100°C[12]. It was found, for instance, that in the absence of oxygen the maximum polymerization rate at first increases with temperature but then reaches a maximum[10] or a plateau and then decreases[11]. This was explained by suppression of autoacceleration due to chain transfer and/or thermally induced unzipping of the kinetic chain[10,11]. Since the final obtainable conversion also passes through a maximum as a function of temperature, it was indicated that thermal stability is the dominant factor in controlling the maximum conversion at high temperatures[11,12].

In most applications the coatings obtained by photopolymerization of di(meth)acrylates should be characterized by good thermal stability, low moisture absorption and, in some cases, high refractive index. All these properties may be improved in comparison to widely used di(meth)acrylates of ethylene glycols and other glycols by the replacement of the ether or $-CH_2-$ group in these monomers by the thioether group. The thermal properties will be improved, since aliphatic sulfides are known to be thermooxidative stabilizers; the moisture absorption will be reduced, since the thioether group is hydrophobic; and the refractive index will be enhanced due to the presence of the strongly polarizable sulfur atom. There are also some indications that the sulfur-containing diacrylates exhibit lower polymerization shrinkage[13].

The aim of this work was to compare the kinetics of the photopolymerization of three model diacrylates containing $-S-$, $-O-$ and $-CH_2-$ linkages in the ester group in order to elucidate the effect of the sulfide group on the reaction course over a wide temperature range. The investigated monomers were: 2,2'-thiobisethanol diacrylate (TEDA), 2,2'-oxybisethanol diacrylate (OEDA) and 1,5-pentanediol diacrylate (PDA).

Because the length of the chain connecting the two



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

TEDA: X=S

OEDA: X=O

PDA: X=CH_2

Table 1 Some properties of the monomers studied

Monomer	MW	Monomer conc.[a] (M)	Purity[b] (%)	d_4^{20} (g ml^{-1})
TEDA	230	4.99	92.1	1.147
OEDA	214	5.18	98.2	1.108
PDA	212	4.87	97.6	1.033

[a] Calculated
[b] By gas chromatography

unsaturations is approximately the same for all three monomers, we may expect that the variations in the reactivities of the monomers studied will result mainly from the chemical reactions occurring at the thioether and ether bonds (especially hydrogen abstraction) but also from some physical factors arising from the monomer structure and caused by the different physical properties of the C–S, C–O and C–C bonds (barrier to rotation, bond strength, polarizability, and so on). Different values of valence angles at –S–, –O– and –C– atoms cause a difference in the shape of monomer molecules and this, together with the different polarities of these groups, may influence the arrangement of the molecules in the bulk, their possible association and the inter- and intramolecular distances between double bonds (the character of association of di(meth)acrylates was found to be very important in their polymerization[14]). All these physical factors may influence the polymerization and, although they will not be taken into account in the discussion of the results presented in this work, we should remember that they may be responsible for some unexplained differences in the behaviours of the investigated monomers during polymerization.

EXPERIMENTAL

The monomers were synthesized by the reaction of appropriate glycols (Merck, Darmstadt) with acroyl chloride (Merck) in the presence of triethylamine (Merck) in dichloromethane (Zakłady Azotowe Kedzierzyn, Poland) solution according to a procedure similar to that described in ref. 15. The characteristics of the monomers are given in *Table 1*.

The polymerization kinetics were monitored by a differential scanning calorimeter (DSC 605 M, Unipan-Termal, Warsaw, Poland) equipped with a lid specially designed for photochemical measurements. As initiator 1-benzoyloxycyclohexanol (BCH; Irganox 184 from Ciba-Geigy, Basel) was applied. The accurately weighed (~ 20 mg) samples of the photocurable composition were polymerized in 6.8 mm diameter open aluminium d.s.c. pans. 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 min at the chosen polymerization temperature. A medium pressure mercury lamp equipped with a glass filter was used for the irradiation. The transmitted light was in the 310–400 nm range with λ_{max} at 366 nm. The incident light intensity at the sample pan position was measured to be 1.8 mW cm^{-2} s^{-1} (by the carbon black method), which corresponds to 5.5×10^{-9} einstein cm^{-2} s^{-1} for 366 nm light. The reflection of the light by the empty aluminium pan was found to be 67%, this reduces the variation in the radiation intensity throughout the sample and enhances the intensity of the light absorbed.

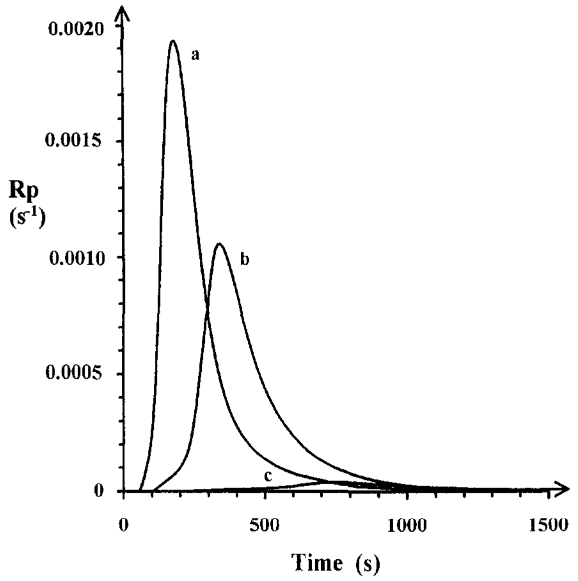


Figure 1 Time–polymerization rate curves of the three diacrylates in air at 40°C: (a) TEDA, (b) OEDA, (c) PDA

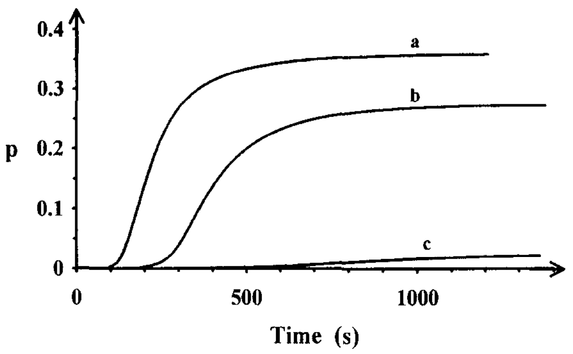


Figure 2 Time–conversion curves of the three diacrylates in air at 40°C: (a) TEDA, (b) OEDA, (c) PDA

For the calculations a value for the heat of polymerization ΔH equal to 86 kJ mol^{-1} was taken. Since the conversion of diacrylates calculated on the basis of $\Delta H = 78$ kJ mol^{-1} (ref. 16), the most often used value, were in some cases higher than 100%, the enthalpy of polymerization was established by fitting the conversion data of the highest conversion levels obtained by d.s.c. to the conversions of the same samples determined by *FT*i.r. This gave the value of about 86–89 kJ mol^{-1}. The value of 86 kJ mol^{-1} was chosen, which still lies in the literature range of acrylates, 78–86 kJ mol^{-1} (ref. 6). The conversion at the time at which the polymerization rate decreased to 0 (~ 20 min) was taken as the final conversion. All the results were analysed for the corrected baseline.

The samples for swelling measurements were prepared by polymerization of 1.5 ml of the monomer under Ar at 30°C in the presence of 0.008 M BCH in vials of 7 mm diameter. The samples were swollen to equilibrium (1 week) at room temperature.

RESULTS AND DISCUSSION

The photopolymerization of the monomers was followed

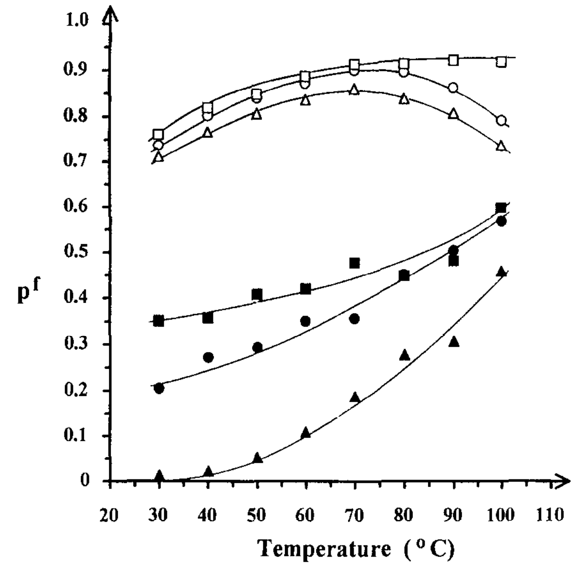


Figure 3 Temperature dependences of final conversions p^f: open symbols denote polymerization in Ar atmosphere; filled symbols denote polymerization in air; (□, ■) TEDA, (○, ●) OEDA, (△, ▲) PDA

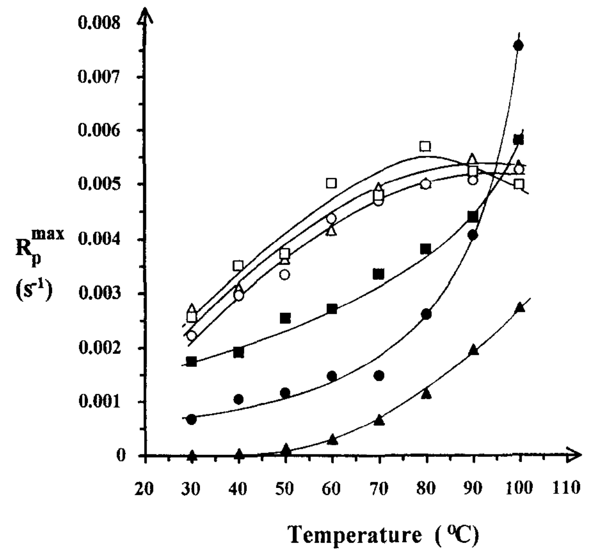


Figure 4 Temperature dependences of maximum polymerization rates R_p^{max}. Symbols as in *Figure 3*

by isothermal d.s.c. in the temperature range of 30–100°C in both neutral (Ar) and air atmospheres. Until now the kinetics of photopolymerization at higher temperatures were considered mainly in the absence of oxygen[8–12]. The observation of the oxygen effect will give better insight into the reactivity of the monomers and the influence of the heteroatom present in the ester group.

The photoinitiator concentration was kept at a level allowing the polymerization to occur slowly enough to observe precisely the temperature effect on the polymerization. It was chosen as 0.04 M for the reactions carried out in air and 0.005 M for those in Ar.

Taking into account the earlier results obtained for dimethacrylates[17] by gravimetry for larger samples, it was expected that the sulfide group would exert a positive effect on the polymerization course at least in air and at moderate temperatures.

Figures 1 and *2* show the time dependences of the polymerization rate R_p (expressed in s^{-1}) and degree of double-bond conversion p (expressed as a fraction) at 40°C in air. It is clearly seen that TEDA polymerizes much faster and to considerably higher conversion than the two other monomers. The same effects are observed in air at lower and medium polymerization temperatures and, only slightly pronounced, in Ar.

The temperature dependences of final conversions p^f, in both air and Ar, are given in *Figure 3*. In air the final conversions increase with temperature and are significantly higher for the heteroatom-containing monomers; TEDA shows the highest p^f values up to about 80°C.

Completely different is the temperature dependence of final conversions in Ar. Up to about 70°C the conversions of all monomers are similar and increase slightly with temperature. Above 70°C p^f of monomers that do not contain sulfur decreases. The existence of a maximum of final conversion at about 80°C or above in the absence of oxygen was observed also by other workers for various di(meth)acrylates[11,12]. However, p^f of the sulfur-containing monomer beyond 70°C remains unchanged, keeping a plateau at least up to 100°C.

Figure 4 illustrates the dependences of the polymerization rates at peak exotherm (maximum polymerization rate R_p^{max}) on curing temperature. In air all the monomers show a steady increase in R_p^{max} with increasing temperature up to 100°C. TEDA is characterized by much higher R_p^{max} values than OEDA and PDA up to 80°C. Above 80°C R_p^{max} of OEDA rapidly increases exceeding at 100°C R_p^{max} of TEDA. In Ar R_p^{max} for the three monomers are very close with slightly higher values for TEDA and increase with temperature only to 80°C. Above this temperature R_p^{max} of OEDA and PDA tend to reach a plateau whereas R_p^{max} of TEDA begins to decrease, reaching at 100°C the values of R_p^{max} lower than those of OEDA and PDA.

So, we observe an interesting phenomenon: the final conversions of OEDA and PDA decrease above 70°C in Ar although their R_p^{max} values still slightly increase, whereas R_p^{max} values of TEDA decrease above 80°C but its p^f values are kept at the highest level reached.

Generally, we can conclude that, whereas the presence of heteroatom influences the reactivity of the monomer in the absence of oxygen rather slightly, it affects deeply the polymerization in air. Much higher reaction rates and p^f values of TEDA and OEDA compared to PDA in air indicate that these monomers are less sensitive to oxygen inhibition and, in turn, the sensitivity of TEDA is much lower than that of OEDA. This result is a consequence of the different rates of consumption of dissolved and diffusing oxygen in the chain peroxidation process:

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

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \qquad (2)$$

where RH is monomer or polymer molecule, $R^\bullet$ is monomer-, polymer- or initiator-derived radical.

Reaction (2) is faster for the heteroatom-containing monomers and is responsible for their reduced sensitivity to oxygen inhibition. However, hydrogen abstraction occurs much easier from the carbon atom attached to sulfur than to oxygen (due to better radical stabilization by S atom[18]); therefore TEDA polymerizes in air faster

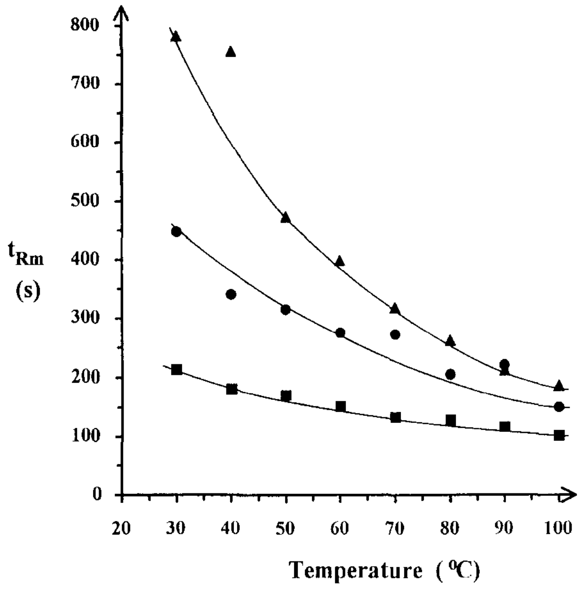


Figure 5 Temperature dependences of times needed to reach R_p^{max} (t_{Rm}) in air. Symbols as in *Figure 3*

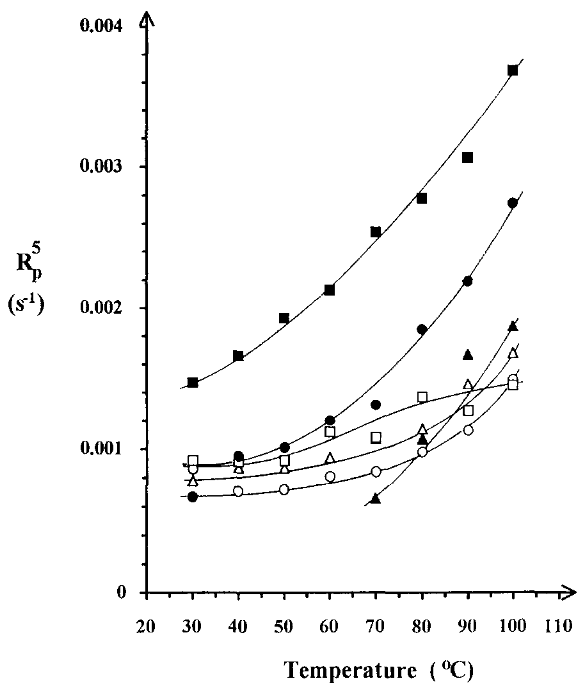


Figure 6 Temperature dependences of the polymerization rates at 5% conversion R_p^5. Symbols as in *Figure 3*

and to higher conversion than OEDA. This reaction may be of lower importance at high initiator concentration, when oxygen is mainly removed in reaction (1) (in this case R• denotes initiator-derived radical).

The lowest sensitivity of TEDA to oxygen inhibition is also manifested by the considerably lower values of the time needed to reach R_p^{max} (t_{Rm}) and the lowest temperature gradient of t_{Rm} (*Figure 5*). However, as will be shown below, the onset and maximum of autoacceleration is affected also by factors other than the retarding effect of oxygen.

The cause of the rapid increase of R_p^{max} of OEDA in air above 70°C is uncertain. It may be connected with a peroxygenation process. The faster reaction (2) for heteroatom-containing monomers causes the concentration of hydroperoxides formed in the reaction to be higher. At temperatures above 70°C the decomposition rate of hydroperoxides and polyperoxides becomes high enough to increase the overall initiation rate. The substantial contribution of hydroperoxides in the initiation of polymerization was indicated in the literature[19]. However, in the case of sulfur-containing monomer, hydroperoxides formed are only intermediate products in the oxidation of sulfur atom[20–22] and cannot participate in the enhancement of the initiation rate (it is impossible, for instance, to reach high conversion of sulfur-containing monomers in the presence of peroxide initiators[23]). As the result, R_p^{max} of OEDA exceeds R_p^{max} of TEDA and their final conversions above 80°C in air become similar. At a low degree of conversion (5%, *Figure 6*) the polymerization rate of OEDA increases with temperature similarly to other monomers, possibly because the concentration of hydroperoxides is still too low to affect the initiation.

Another reaction that influences the course of polymerization, and its effects should be especially visible in the absence of oxygen is the chain-transfer reaction:

$$\sim M^\bullet + RH \rightarrow \sim MH + R^\bullet \qquad (3)$$

where $\sim M^\bullet$ is a macroradical and RH is a monomer or polymer molecule.

Participation of this reaction is significant in the polymerization of acrylates due to the presence of tertiary hydrogens in the polymer backbone[1]. Such reaction (by tertiary hydrogens) should occur to a similar degree for poly-TEDA, poly-OEDA and poly-PDA. However, the chain-transfer constants for hydrogens in a CH_2 group attached to sulfur atom are considerably higher than those for hydrogens in a CH_2 group attached to oxygen atom and higher than for tertiary hydrogens[16]. Therefore, the influence of the following reaction:

$$\sim M^\bullet + -CH_2-S- \rightarrow \sim MH + -{}^\bullet CH-S- \qquad (4)$$

may be appreciable during the photopolymerization of TEDA.

The general consequence of reaction (3) is grafting leading to formation of more dense polymer network and the acceleration of termination by introduction of some mobility to radical sites attached to the network[1]. Owing to reaction (4) both these processes will occur to a higher degree of TEDA and since the activation energy of the chain-transfer reaction is higher than that of the propagation process by 20–40 kJ mol^{-1} with active transfer agents[16], its contribution will be greater at higher temperatures. The formation of considerable amounts of –•CH–S– radicals reduces the polymerization rate not only by enhanced termination but also due to slower reinitiation caused by lower reactivity of radicals stabilized by sulfur. Therefore, we observe the drop of R_p^{max} of TEDA above 80°C in Ar.

It is interesting to note that at such a low conversion level as 5% (*Figure 6*), the polymerization rate in Ar increases with temperature and, in contrast to R_p^{max}, for OEDA and PDA does not tend to reach a plateau above 70°C. However, for TEDA the increase of R_p^5 with temperature is hampered above 80°C. This leads to the conclusion that the decelerating processes influencing R_p^{max} above 80°C result from two main factors: one that depends and another one that does not depend on the conversion

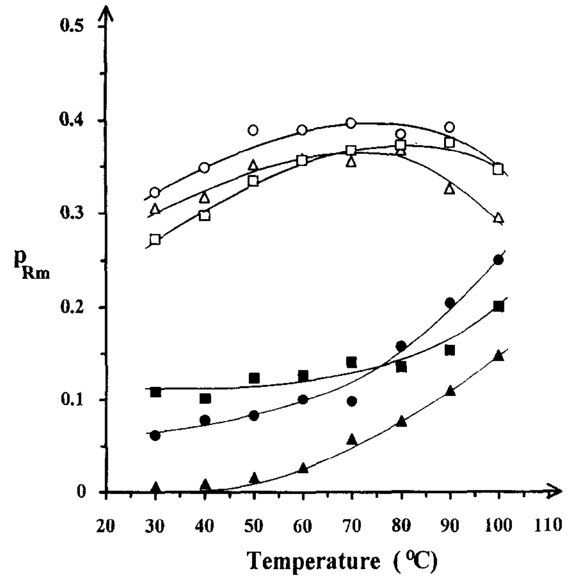


Figure 7 Temperature dependences of conversions at R_p^{max} (p_{Rm}). Symbols as in *Figure 3*

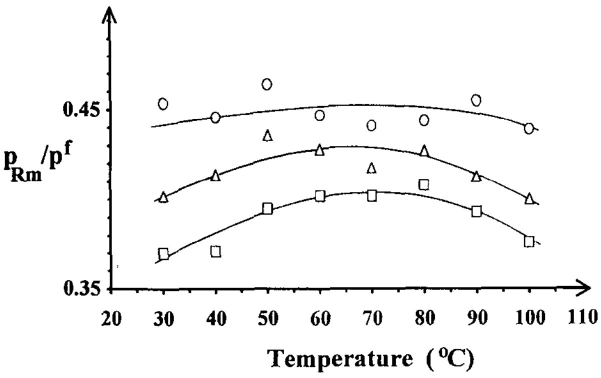


Figure 8 Temperature dependences of ratios p_{Rm}/p^f in Ar. Symbols as in *Figure 3*

level achieved. The first factor may be chain transfer to polymer and/or polymer degradation and may explain the difference between the temperature dependences of R_p^5 and R_p^{max} in Ar for OEDA and PDA. The second factor, which affects the polymerization rate of TEDA just from the early polymerization stages, is chain transfer to monomer and polymer according to reaction (4).

One of the factors that characterizes the autoacceleration is the degree of conversion at which R_p^{max} is reached (p_{Rm}). Its temperature dependence in both Ar and air is shown in *Figure 7*. Although p^f values for TEDA in Ar are a little higher than for other monomers, its p_{Rm} are the lowest, at least to about 70°C. Since, beginning from this temperature, p^f for OEDA and PDA decreases, it is better to consider what fraction of final conversion p_{Rm} makes, i.e. the ratio p_{Rm}/p^f (*Figure 8*). In Ar this ratio is the lowest for TEDA in the whole temperature range and may be caused by the following effects. At the early polymerization stages chain transfer favours grafting rather than termination; therefore, in TEDA gelation sets in earlier and results in earlier occurrence of autoacceleration. However, at further polymerization stages, when termination instead of being controlled by translational diffusion (which brings the radicals together) becomes controlled by reaction diffusion (when two radicals are brought into contact by a series of propagation steps[11]), the chain transfer enhances termination by mobilization of trapped radicals and is responsible for earlier deceleration in TEDA.

Although crosslinking accelerates polymerization initially at lower conversions, it ultimately restricts radical chain and monomer diffusion at higher percentages of conversion as the network crosslink density increases. For this reason the final conversion will depend mainly on the network mobility, and the fact that the extents of conversion of the polymerization occurring under deceleration conditions beyond R_p^{max} are higher for TEDA may be caused by the higher flexibility of diacrylate spacer group due to lower barrier to rotation of the C–S bond[23].

The importance of the chain-transfer reaction in the polymerization of dimethacrylates[24] and diacrylates[25] in both air and Ar was shown for the formulations containing various sulfide additives and the scheme of the action of sulfides was proposed[25].

As was mentioned earlier, the maximum on the plot of final conversion vs. temperature as well as the maximum or a plateau on the plot of R_p^{max} vs. temperature were explained by the depropagation of the polymer formed and/or by decelerating effect of chain-transfer reaction[10–12]. The chain-transfer reaction will be the most pronounced in TEDA polymerization and, since p^f of TEDA does not show a maximum, chain transfer cannot be the cause of the decrease of p^f above 70°C observed for PDA and OEDA in Ar. Moreover, polyacrylates do not undergo depropagation since chain transfer to polymer backbone occurs and thermal decomposition of polyacrylates is initiated by breaking of the bond at the radical formed after abstraction of tertiary hydrogen from the polymer chain[26]. However, if we accept the explanation by thermal instability but in the form of polymer degradation and not depolymerization, we should also assume that the thioether bond, by chain transfer competitive to that from polymer backbone, exerts a stabilizing effect on the polymer protecting it from degradation in Ar. The apparent lack of polymer degradation in the presence of atmospheric oxygen may result in part from the fact that the thermal effect observed by d.s.c. is a result of various processes occurring simultaneously to a higher or lesser degree, e.g. exothermic oxygenation and polymerization, endothermic degradation or others. For better explanation a comparison with other methods is needed.

The presence of a heteroatom in a polymer may affect its swelling properties. The degree of double-bond conversion of the samples of poly-TEDA, poly-OEDA and poly-PDA prepared for swelling measurements should be similar (compare *Figure 3*) and the swelling of polymers should reflect mainly the difference in their crosslink densities, which do not derive from p^f value, as well as the compatibility of the polymers with the solvent used (*Table 2*). Generally, poly-TEDA is least susceptible

Table 2 Swelling of polymers (wt%)

Polymer	Water	Toluene
poly-TEDA	1.4	0.5
poly-OEDA	1.9	0.5
poly-PDA	1.5	2.4

to solvent penetration. The hydrophilicity of the ether bond probably makes poly-OEDA the most swellable in water; the swelling of poly-TEDA and poly-PDA is similar with the lower value for the former. In toluene, in turn, the swelling of poly-TEDA and poly-OEDA is the same and about six times lower than that of poly-PDA. The lowest swellability of poly-TEDA makes it useful for potential applications in protective coatings.

The consideration of the temperature effect on the course of polymerization needs also calculation of activation energies (E_a). The final shapes of Arrhenius plots depend not only on the thermal dependence of R_p but also on other processes influencing the polymerization rate and having their own activation energies, such as decomposition of polymer or peroxides, chain transfer, oxygen consumption and diffusion as well as on temperature gradients of viscosity and oxygen solubility. Therefore, the clear linear dependence may be disturbed and the obtained apparent E_a values may be affected to a degree depending on the contribution and importance of particular processes.

The usual expression for the activation energy is given by the relation (5):

$$E_a = E_p + 0.5E_i - 0.5E_t \qquad (5)$$

where E_p is activation energy of propagation, E_i is activation energy of initiation and E_t is activation energy of termination.

In the case of photochemical initiation:

$$E_a = E_p - 0.5E_t \qquad (6)$$

since E_i is small or zero. However, expression (6) was derived for bimolecular termination when k in the Arrhenius equation:

$$k = A\ \exp(-E_a/RT) \qquad (7)$$

is determined by the relation:

$$R_p = k[\mathrm{M}] \qquad (8)$$

in which k, for photochemical initiation, is expressed by[6]:

$$k = k_p/(k_t^b)^{0.5}\Phi(I_a)^{0.5} \qquad (9)$$

where k_p = propagation rate constant, k_t^b = bimolecular termination rate constant, Φ = quantum yield of initiation, I_a = intensity of absorbed light and [M] = concentration of double bonds.

Expression (9) was derived under steady-state assumption. In the polymerization of multifunctional monomers a steady state practically does not occur and the contribution of monomolecular termination may be appreciable from the early polymerization stages. Therefore, we cannot use equation (6) to determine the possible relation between E_p and E_t, as we sometimes find in the literature, before we are sure that the steady state and bimolecular termination really take place. Both these conditions are not fulfilled in the polymerization described in this work.

Calculation of E_a at R_p^{max} should be performed on the basis of the composite rate constant k (equation (8)), namely $R_p^{max}/(1\text{-}p_{Rm})$, since the double-bond concentration at R_p^{max} varies with temperature (compare *Figure 7*). At R_p^{max} the propagation reaction is under a mixture of chemical and diffusional control and also diffusion effects will influence the calculated E_a.

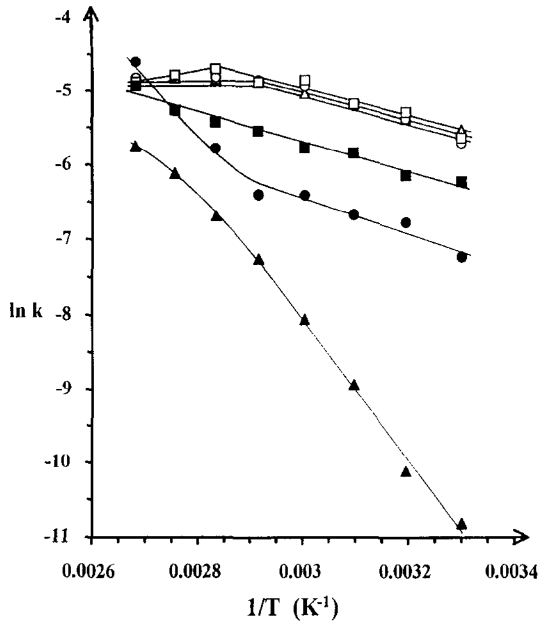


Figure 9 Arrhenius plots of the composite rate constants k at R_p^{max}. Symbols as in *Figure 3*

Table 3 Apparent activation energies at R_p^{max} for TEDA, OEDA and PDA polymerization calculated for the composite rate constants

	Ar		Air	
Monomer	Temp. range (°C)	E_a (kJ mol^{-1})	Temp. range (°C)	E_a (kJ mol^{-1})
TEDA	30–80	16	30–100	17
	80–100	−10		
OEDA	30–70	19	30–70	18
	70–100	1	70–100	63
PDA	30–70	15	30–70	80
	70–100	−0.1	70–100	54

In addition to the factors listed above, other inaccuracy in determination of E_a derives from the fact that relation (8) assumes a first-order dependence of R_p on monomer concentration. However, the reaction order is very often higher than unity[6,16] and this is also the case for the investigated monomers under the conditions used in this work. Despite this, in this paper E_a has been calculated on the basis of equations (7) and (8) to enable the comparison of the results with those obtained by other authors.

Arrhenius plots of k at R_p^{max} for polymerization carried out in air and in Ar are given in *Figure 9*. Generally on the plots obtained for Ar atmosphere we can distinguish two regions: up to about 70–80°C and above, in which the plots are almost linear but E_a values obtained for these regions differ substantially (*Table 3*). In the first region E_a values for all the monomers are in the range of 14–19 kJ mol^{-1} (these values correspond with the literature data for various di(meth)acrylates) and in the second one become very low, near zero for OEDA and PDA and markedly negative in the case of TEDA. The existence of two regions was also observed by other workers[9,10] and a value of E_a near zero and negative for the second region was explained by enhanced termination due to chain transfer by tertiary hydrogens from polyacrylate backbone[10] or as a consequence of decreasing tendency of polymerization rates caused by depropagation of the kinetic chain[11]. Enhanced chain transfer may be responsible for the negative value of E_a for TEDA but, as was indicated above, we cannot take depropagation into account.

The E_a values obtained for polymerization in air are close to those in Ar for TEDA and OEDA up to 70°C (TEDA shows only one value of E_a) and we can conclude that in these cases the presence of oxygen does not significantly influence E_a. Only one value of E_a in air in the whole temperature range for TEDA indicates that the retarding processes occurring above 80°C (observed in Ar) are balanced by the accelerating effect of faster oxygen consumption caused by the sulfide group. The rapid increase of E_a above 70°C for OEDA reflects the increase of its R_p^{max} and the high value of E_a indicates the occurrence of a thermal process, possibly decomposition of hydroperoxides. Very high E_a values for PDA in air indicate in turn a very strong influence of oxygen on the polymerization, especially at lower temperatures. Also in this case at higher temperatures the formation of hydroperoxides may assist the initiation.

CONCLUSIONS

The sulfide group introduced into an acrylate monomer exerts a positive effect on the photopolymerization course in both air and Ar. It markedly lowers the monomer sensitivity to oxygen inhibition and prevents the drop of final conversion (as measured by d.s.c.) in Ar at higher temperatures. The action of the sulfide group is based on hydrogen abstraction from CH_2 attached to sulfur, which causes faster oxygen consumption (both dissolved and diffusing), enhances network density, increases the mobility of radical sites and is competitive to abstraction of tertiary hydrogens from the polymer backbone by growing macroradical.

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REFERENCES

1 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1

2 Pappas, S. P. (Ed.) 'Radiation Curing: Science and Technology', Plenum Press, New York, 1992, Ch. 5–9

3 Scranton, A. B., Bowman, C. N., Klier, J. and Peppas, N. A. *Polymer* 1992, **33**, 1683; Anseth, K. S., Bowman, C. N. and Peppas, N. A. *J. Polym. Sci. (A) Polym. Chem.* 1994, **32**, 139

4 Decker, C. in 'Radiation Curing in Polymer Science and Technology' (Eds. J. P. Fouassier and J. F. Rabek), Vol. III, Elsevier Applied Science, London, 1993, p.33

5 Müller, V., Jockusch, S. and Timpe, H. -J. *J. Polym. Sci. (A) Polym. Chem.* 1992, **30**, 1755

6 Hoyle, C. in ref. 2, Ch. 3

7 Decker, C. in ref. 2, Ch. 4

8 Tryson, G. R. and Schulz, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 2059

9 Doornkamp, A. T. and Tan, Y. Y. *Polym. Commun.* 1990, **31**, 362

10 Broer, D. J., Mol, G. N. and Challa, G. *Polymer* 1991, **32**, 690

11 Cook, W. D. *Polymer* 1992, **33**, 2152

12 Cook, W. D. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 1053

13 Sherman, A. M., 10th Conf. Proc: RADCURE '86, 13–25 April 1986

14 Sukhareva, L. A. 'Poliefirnye Pokrytya, Struktura i Svoistva', Khimiya, Moskva, 1987

15 Lin, M. S. and Jeng, K. T. *J. Polym. Sci. (A) Polym. Chem.* 1992, **30**, 1941

16 Odian, G. 'Principles of Polymerization', 2nd Edn., Wiley, New York, 1981

17 Andrzejewska, E. and Andrzejewski, M. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 2365

18 Neville, D. (Ed.) 'Comprehensive Organic Chemistry', Vol. 3, Pergamon, New York, 1979, p. 34

19 Decker, C. and Moussa, K. *J. Appl. Polym. Sci.* 1987, **34**, 1603

20 Scott, G. in 'Developments in Polymer Stabilization' (Ed. G. Scott), Vol. 4, Applied Science, London, 1981, p.1

21 Shelton, J. R. in 'Developments in Polymer Stabilization' (Ed. G. Scott), Vol. 4, Applied Science, London, 1981, p. 23

22 Scott, G. in 'Developments in Polymer Stabilization' (Ed. G. Scott), Vol. 6, Applied Science, London, 1983, p. 29

23 Rabie, A. M. *Eur. Polym. J.* 1972, **8**, 687

24 Andrzejewska, E. and Andrzejewski, M. *Polimery (Warsaw)* 1994, **39**, 22

25 Andrzejewska, E. *Polymer* 1993, **34**, 3899

26 David, C. in 'Comprehensive Chemical Kinetics' (Ed. C. H. Bamford), Vol. 14, Elsevier Scientific, Amsterdam, 1975, p. 62