

polymer communications

Sulfur-containing polyacrylates: VI. Temperature effects on the photoinitiated polymerization of dimethacrylates

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The polymerization of three analogous monomers—2,2'-thiobisethanol dimethacrylate, 2,2'-oxybisethanol dimethacrylate and 1,5-pentanediol dimethacrylate—has been studied in the temperature range 30–95°C by isothermal d.s.c. The temperature and heteroatom effects on the polymerization course were considered from the point of view of the occurrence and relative importance of hydrogen abstraction reaction which is manifested by chain transfer and chain peroxidation processes. Generally the advantageous effect of the sulfide group is revealed in reduction of oxygen inhibition and suppression of the drop of final conversion with increasing temperature above 70°C in the absence of oxygen. However, the influence of the sulfide group on the polymerization of dimethacrylates is not so great as on diacrylates due to various factors of both a physical and chemical nature.

(Keywords: dimethacrylates; sulfide group; temperature effect on photopolymerization)

Introduction

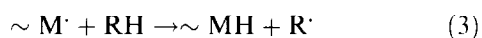
In the preceding paper concerning the influence of temperature on the photoinitiated polymerization of diacrylates¹ it was shown that the most important differences in the polymerization kinetics of the analogous monomers differing only by the presence or type of the heteroatom in the ester group result from the occurrence and relative importance of the following reactions:

– oxygen consumption in a chain peroxidation process



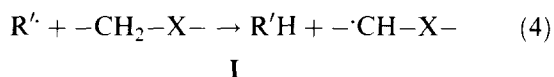
where RH is monomer or polymer molecule, R[·] is monomer, polymer or initiator deriving radical:

– chain transfer to monomer or polymer



where $\sim M\cdot$ is macroradical.

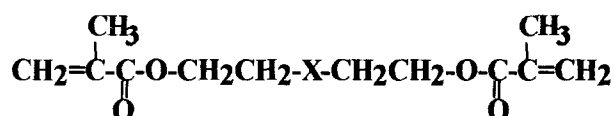
In the case of heteroatom-containing monomers hydrogen abstraction occurs mainly at the CH₂ group attached to the heteroatom:



where X is the heteroatom (S or O), R'[·] is ROO[·], $\sim M\cdot$ or initiator deriving radical.

For a sulfur-containing monomer, reaction (4) is faster and of greater importance than for an oxygen-containing analogue, since aliphatic sulfides are better chain transfer agents² and form better stabilized radical I than ethers³. As the main result a suppression of oxygen inhibition occurs and the polymer sensitivity to thermal degradation is reduced.

This paper concerns the temperature effect on the photoinitiated polymerization of three analogous dimethacrylates from the point of view of the contribution and the influence of reactions (2) and (3) and compares the importance of these reactions in the polymerization of dimethacrylates and diacrylates. The investigated monomers were: 2,2'-thiobisethanol dimethacrylate (TEDM), 2,2'-oxybisethanol dimethacrylate (OEDM) and 1,5-pentanediol dimethacrylate (PDM).



TEDM: X=S

OEDM: X=O

PDM: X=CH₂

Experimental

The monomers were synthesized by the transesterification of methyl methacrylate (Zakłady Chemiczne Oświęcim, Poland) with the appropriate glycol (Merck, Darmstadt) in a solvent-free process in the presence of sodium methoxide (Merck) as described in ref. 4. The characteristics of the monomers are also given in ref. 4. The purity of the monomers exceeded 96%.

The polymerization kinetics were monitored by a differential scanning calorimeter (DSC 605 M, UNIPAN-TERMAL, Warsaw) according to a procedure described in ref. 1. The sample weight was 20 mg and the incident light intensity used (from a medium-pressure Hg lamp, 310–400 nm range, $\lambda^{\text{max}} = 366 \text{ nm}$) was 1.8 mW cm^{-2} . As initiator 1-benzoyloxycyclohexanol (BCH, Irganox 184 from Ciba-Geigy, Basel) was applied. For the

calculations the enthalpy of polymerization was taken as equal to 56 kJ mol^{-1} (ref. 2). The conversion at the time at which the polymerization rate decreased to 0 ($\sim 20 \text{ min}$) was taken as the final conversion. All the results were analysed for the corrected base line.

Results and discussion

The polymerization of monomers was followed by isothermal d.s.c. in the temperature range $30\text{--}95$ (100) $^{\circ}\text{C}$ both in Ar and air atmospheres. The photoinitiator concentration 0.01 M was the same in air and Ar and allowed the polymerization to occur slowly enough to observe precisely the effect of temperature.

To characterize the polymerization course the following parameters were determined for each monomer and temperature from the d.s.c. data: the final conversion of double bonds (p^f , expressed as a fraction), the maximum polymerization rate (R_p^{\max} , in s^{-1}), conversion at R_p^{\max} (p_{Rm}), time needed to reach R_p^{\max} (t_{Rm}), polymerization rate at 5% conversion (R_p^5) and activation energies.

Figures 1 and 2 present the time dependencies of the polymerization rate R_p and degree of double bond conversion p at 40°C in air. Under these conditions TEDM polymerizes much faster and to much larger conversions than the two other monomers. A similar situation exists in the whole temperature range as is shown by p^f -temperature and R_p^{\max} -temperature plots (Figures 3 and 4). These results may be explained by faster oxygen consumption (both dissolved and diffusing to TEDM) in reactions (1) and (4) (when R^{\cdot} is ROO^{\cdot}).

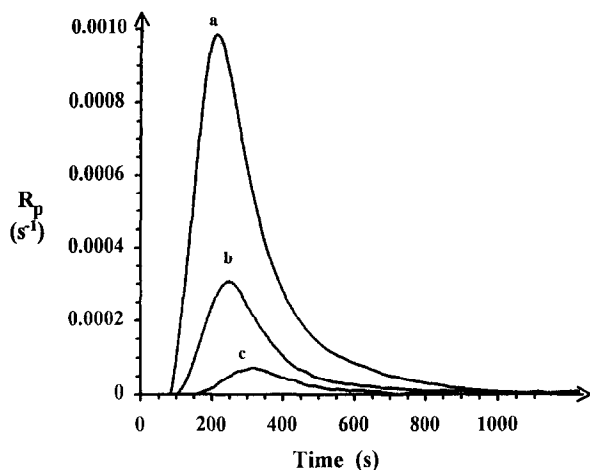


Figure 1 Time-polymerization rate curves of the three dimethacrylates in air at 40°C : (a) TEDM, (b) OEDM, (c) PDM

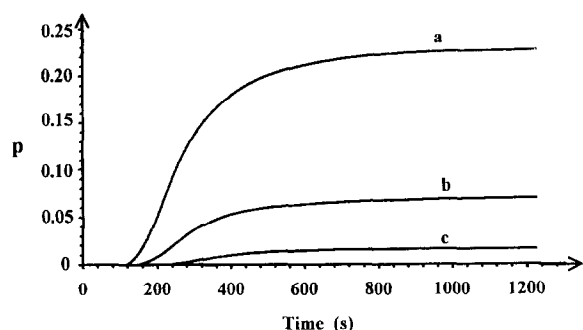


Figure 2 Time-conversion curves of the three dimethacrylates in air at 40°C : (a) TEDM, (b) OEDM, (c) PDM

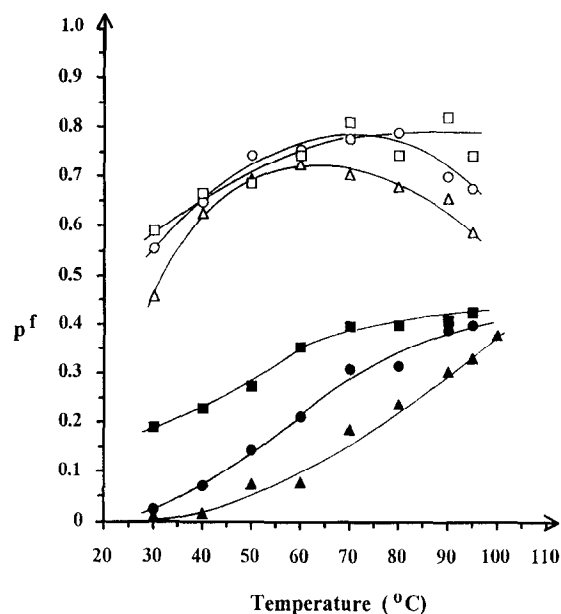


Figure 3 Temperature dependencies of final conversions p^f . Open symbols denote polymerization in Ar atmosphere, filled symbols denote polymerization in air. \square , \blacksquare TEDM; \circ , \bullet OEDM; \triangle , \blacktriangle PDM

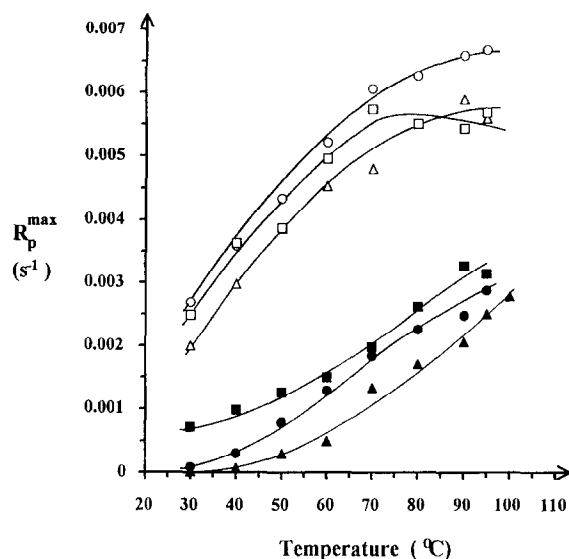


Figure 4 Temperature dependencies of maximum polymerization rates R_p^{\max} . Symbols as in Figure 3

Reactions (1) and (4) also reduce sensitivity to oxygen inhibition of OEDM but not to so high degree as for TEDM.

In Ar p^f and R_p^{\max} values for all the monomers are similar with somewhat higher values for the heteroatom-containing monomers. Up to about 70°C these parameters increase with temperature. The further increase of the polymerization temperature in Ar produces a similar effect on p^f (Figure 3) and R_p^{\max} (Figure 4) for dimethacrylates as for analogous diacrylates¹: the final conversions of OEDM and PDM drop down above about $60\text{--}70^{\circ}\text{C}$ despite the fact that their R_p^{\max} still slightly increases whereas p^f values of TEDM are kept at an almost constant level though its R_p^{\max} values slightly decrease above 70°C .

A similarity to diacrylates also occurs in the temperature dependence of R_p at the low conversion level of 5%

(Figure 5) in Ar. In contrast to R_p^{\max} , the increase of R_p^5 with temperature for OEDM and PDM is not hampered above 70°C. However, for TEDM the increase of its R_p^5 value with temperature is markedly reduced beyond 70°C showing a similarity to its R_p^{\max} behaviour. This leads us again to the conclusion¹ that the temperature influence on the polymerization rate results from two main factors: one which depends and another one which does not depend on the conversion level of double bonds.

The temperature tendencies of p_{Rm} in air and Ar are near those of final conversions (Figure 6) except for that of TEDM in Ar which is connected with the drop of its R_p^{\max} above 70°C.

In the absence of oxygen the importance of the chain transfer reaction (reaction (3)) increases. Its consequence is an enhancement of crosslink density due to grafting and acceleration of termination by mobilization

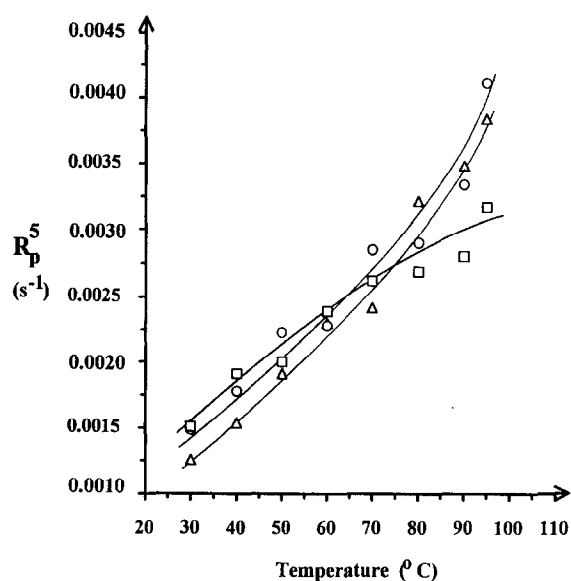


Figure 5 Temperature dependencies of polymerization rates at 5% conversion R_p^5 in Ar. Symbols as in Figure 3

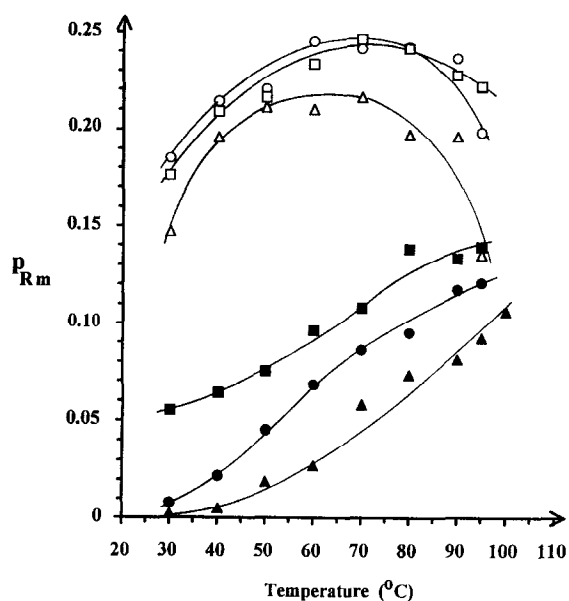


Figure 6 Temperature dependencies of conversions at R_p^{\max} (p_{Rm}). Symbols as in Figure 3

of trapped radicals⁵. Since the activation energy of chain transfer is higher than that of propagation by 20–40 kJ mol⁻¹ (ref. 2), its contribution will be greater at higher temperatures. Reaction (3) will exert the deepest influence on TEDM polymerization. In addition to enhanced termination, the formation of considerable amounts of $\cdot\text{CH-S}$ radicals (both from monomer and polymer molecules) reduces the polymerization rate due to slower reinitiation caused by lower reactivity of radicals stabilized by sulfur⁶. Enhanced termination and slower reinitiation may explain the retardation of the temperature increase of both R_p^5 and R_p^{\max} of TEDM in Ar above 70°C.

Another aspect of reaction (3), the introduction of branching from the early polymerization stages, should accelerate the onset of the gel effect. In the case of dimethacrylates the effect of earlier gelation is less pronounced as for diacrylates due, probably, to the higher stiffness of the methacrylate backbone and lower chain transfer constants of methacrylate radical⁷. This effect is only slightly marked as a reduction of t_{Rm} of TEDM in comparison to OEDM and PDM below 50°C (Figure 7). More visible is the retarding influence of chain transfer which makes t_{Rm} of TEDM the longest above 70°C both in Ar and air despite the fact that R_p^{\max} of TEDM in air is still the highest as the result of faster oxygen consumption.

The higher stiffness of the methacrylate backbone as well as the lower sensitivity of methacrylates to oxygen inhibition⁸ may be the reason that the other slightly accelerating processes (lower barrier to rotation of the C–S bond which makes the dimethacrylate spacer group more flexible⁴, decomposition of peroxides formed) have almost no influence on the polymerization.

As was mentioned earlier, the final conversions of OEDM and PDM in Ar pass through a maximum at about 60–70°C, whereas p^f of TEDM practically

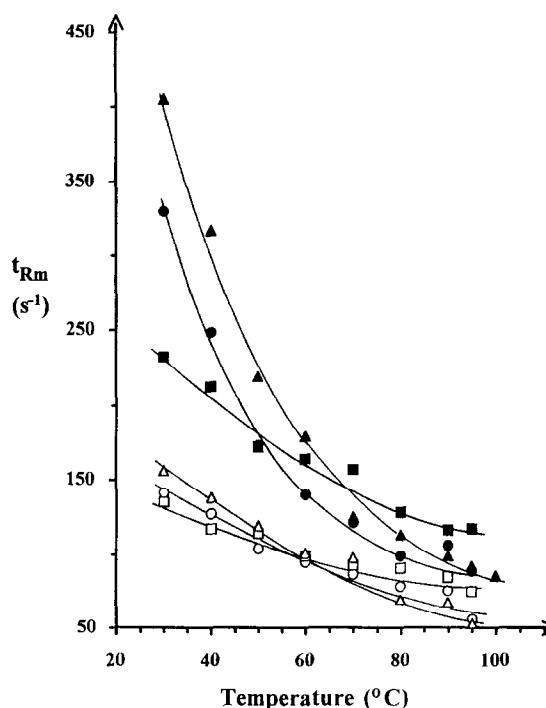


Figure 7 Temperature dependencies of the time needed to reach R_p^{\max} (t_{Rm}). Symbols as in Figure 3

remains unchanged above 70°C. The existence of a maximum on the plot of final conversion vs. temperature for the polymerization carried out in an inert atmosphere was observed for various dimethacrylates and diacrylates by other authors and the decelerating effects of chain transfer reaction and/or thermal stability of the polymer chain were indicated to be the factors controlling p^f and R_p^{\max} at high temperatures⁹⁻¹¹. The main method of degradation of polymethacrylates is depolymerization, the contribution of which depends on the ester group structure^{12,13}. We found earlier that the high temperature degradation of poly-OEDM leads to depolymerization in a high degree whereas in the case of poly-TEDM the monomer is only the minor (~3%) product due in part to chain transfer reaction¹². Since depolymerization begins from the radical end of the polymer chain, the chain transfer according to reaction (4) with the formation of stabilized radical I will counteract depropagation. In this way the substantial contribution of reaction (4) in the polymerization of TEDM prevents the polymer depropagation which probably occurs in the case of poly-OEDM and poly-PDM. Thermal instability of the polymer formed could explain the different temperature dependence of R_p^5 and R_p^{\max} of OEDM and PDM: at medium conversions as at R_p^{\max} , the polymerization rate observed is a result of exothermic polymerization and endothermic depolymerization processes; at low (5%) conversion the propagation is favoured and R_p^5 increases with temperature with no tendency to retardation as in the case of R_p^{\max} .

We may also try to explain the apparently better thermal stability of polymers in air by the competition between endothermic and exothermic (in this case additionally oxygenation) processes resulting in the thermal effect observed. As indicated above, the contribution of these processes varies with temperature and degree of conversion (lower under air than argon).

In our previous study concerning photo- and thermally initiated polymerization of TEDM, OEDM and PDM⁴ we observed the polymerization course by gravimetry. We found that at 75°C in air the polymer yields of OEDM and PDM after reaching their maximum values began to decrease with increasing the polymerization time, indicating a degradative process. The drop of the polymer yield was not observed for TEDM at 75°C and at lower temperatures for all the monomers. This observation is in agreement with the results obtained in this work despite the difference in the variable measured (polymer yield vs. double bond conversion) and in the polymerization atmosphere (for larger and thicker samples used in gravimetric measurements oxygen diffusion plays a less important role).

Continuing the comparison of the results obtained by gravimetric and d.s.c. methods we may conclude that both methods give qualitatively similar results and the differences in the magnitude of the effect of the sulfide group may derive both from the difference in the parameters characterizing the polymerization¹⁴, polymerization conditions and from the fact that the actual polymerization temperature of larger samples is probably higher than that of the thermostatting medium due to difficulties in carrying away the polymerization heat.

The calculations of the apparent activation energies (E_a) were performed for R_p^{\max} (in Ar and air) and for R_p^5 (only in Ar, because in air R_p^5 values are beyond or close

to R_p^{\max}) on the basis of the composite rate constant $k = R_p/(1-p)$. This relation assumes first-order dependence of R_p on monomer concentration ($1-p$) and although it is not the case under the polymerization conditions used in this work it was applied to enable comparison with the results obtained by other authors. In the polymerization of multifunctional monomers the contribution of monomolecular termination is significant and we cannot consider the possible relation of activation energy of propagation (E_p) and termination (E_t) on the basis of the equation:

$$E_a = E_p - 0.5E_t \quad (5)$$

(activation energy of photoinitiation is close to 0)

Arrhenius plots of k at R_p^{\max} for the polymerization carried out in air and Ar are given in Figure 8. Some of them show visible deviation from linearity indicating an influence of disturbing processes and simplifications used in determination of E_a (ref. 1). However, in an approximation, we can distinguish two regions on these plots: up to 70°C and above this temperature. The corresponding average E_a values are given in Table 1. In Ar at lower temperature regions E_a values of the three monomers are very close and correspond to the values cited for various methacrylates (for instance refs 2 and 9). Above 70°C E_a drops to values near zero or even negative. So low activation energies for OEDM and PDM obtained in spite of increasing temperature tendency of their R_p^{\max} are the result of increasing ($1-p_{R_m}$) values above 70°C which cause different temperature dependencies of R_p^{\max} and k . We can try to explain this behaviour of activation energies by the thermal depropagation in the case of OEDM and PDM and enhanced chain transfer in the case of TEDM.

The activation energies obtained for the polymerization of OEDM and PDM in air are very high, especially in the lower temperature region and indicate very strong retardation by oxygen at the photoinitiator concentration

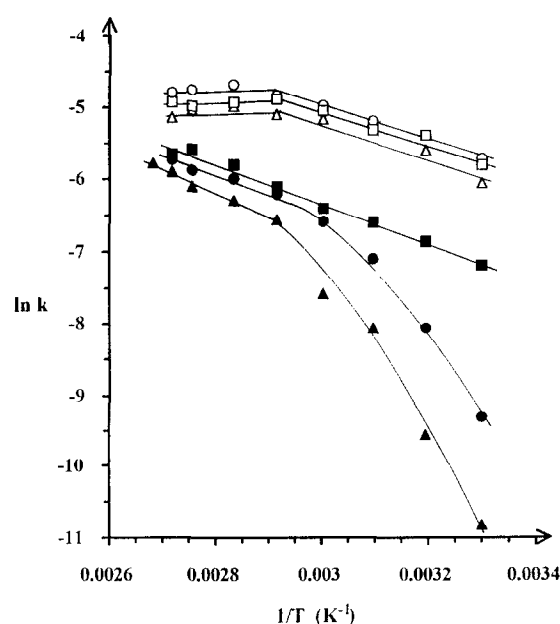


Figure 8 Arrhenius plots of the composite rate constants k at R_p^{\max} . Symbols as in Figure 3

Table 1 Apparent activation energies at R_p^{\max} and R_p^5 for TEDM, OEDM and PDM polymerizations calculated from the composite rate constants

Monomer	R_p^{\max} , Ar		R_p^{\max} , air		R_p^5 , Ar	
	Temp. range (°C)	E_a (kJ mol ⁻¹)	Temp. range (°C)	E_a (kJ mol ⁻¹)	Temp. range (°C)	E_a (kJ mol ⁻¹)
TEDM	30-70	19	30-95	23	30-70	12
	70-95	-3			70-95	7
OEDM	30-70	19	30-60	77	30-95	13
	70-95	1	70-95	19		
PDM	30-70	21	30-70	91	30-95	16
	70-95	-1	70-100	28		

used. Only one E_a value for TEDM in the whole temperature range is close to that obtained in Ar and again proves that the sulfur-containing monomer is much less sensitive to oxygen inhibition.

On the other hand, Arrhenius plots of k at R_p^5 in Ar are linear and show only one value for OEDM and PDM in the whole temperature range (Table 1). This confirms that the decelerating processes occurring beyond 70°C are connected rather with the conversion level of unsaturated functionalities. The E_a values are somewhat lower than those at R_p^{\max} which indicates the influence of the diffusion effects on the polymerization rates at cure extents near p_{Rm} . However, for TEDM we obtain two E_a values. Apparent activation energy in the region above 70°C is lowered in relation to that below 70°C but not in so high degree as in the case of R_p^{\max} . Therefore, we can conclude that the retarding effect of chain transfer is much more pronounced in more viscous media at higher conversions where apart from slower reinitiation the enhanced termination affects the polymerization.

Conclusions

The most important result of the introduction of the sulfide group into a dimethacrylate monomer is the reduction of monomer sensitivity to oxygen inhibition which allows much higher conversions and reaction rates to be reached. In the absence of oxygen the sulfide group prevents the decrease of final conversion (as measured by d.s.c.) above 70°C at least to ~100°C. In comparison to diacrylates the lower susceptibility of dimethacrylates to oxygen inhibition has the result that the beneficial effect of the sulfide group on the polymerization rate in air is not so large as in the case of diacrylates. Moreover, due to the higher stiffness of the methacrylate backbone, the polymerization of dimethacrylates is less susceptible to slightly accelerating processes, especially of a physical nature, like earlier gelation due to chain transfer or

increase of the elasticity of di(meth)acrylate spacer group as the result of a lower barrier to rotation of the C-S bond. For these reasons the retarding processes in the polymerization of dimethacrylates are relatively more pronounced and set in earlier than in the polymerization of diacrylates. The lower effect of the sulfide group on the polymerization of methacrylates than on acrylates may also result from the fact that the chain transfer constants of methacrylate radicals are several times lower than those for acrylate radicals⁷.

Acknowledgement

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- 14 The conversion of double bonds is always lower than the final polymer yield and these two quantities are not proportional to each other since two polymer samples of the same weight may possess different amounts of pendent double bonds